THE SCIENCE OF RUBBER

("Handbuch der Kautschukwissenschaft")

Edited by

PROF. DIPL.-ING. K. MEMMLER

PROFESSOR OF THE STAATLICHE MATERIALPRUFUNGSAMT AT BERLIN-DAHLEM
AND DOZENT AT THE TECHNISCHE HOCHSCHULE, BERLIN
IN COLLABORATION WITH

L. Hock
E. Kindscher
A. Koch
H. Pohle
R. Pummerer
A. Schob
A. Zimmermann

Authorized English Translation

Edited by

R. F. Dunbrook, Ph. D.

AND

V. N. Morris, Ph. D.

OF THE RESEARCH STAFF OF THE FIRESTONE TIRE & RUBBER COMPANY
IN COLLABORATION WITH
THE FOLLOWING MEMBERS OF THE FIRESTONE RESEARCH LABORATORIES:

H. P. Albaugh
H. P. Coats
E. O. Edelmann
H. W. Greenup
J. H. Howey
N. Johnston
F. L. Kilbourne
E. F. Scheffler
N. A. Shepard
J. E. Whittenberg

BOOK DEPARTMENT

REINHOLD PUBLISHING CORPORATION

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Translators' Preface

When Memmler's "Handbuch der Kautschukwissenschaft" first came to the attention of the translators, they were immediately impressed by the fact that no book in English covered the subject of rubber so fully from the scientific point of view. Although good books have been written in English on plantation practice and on the technology of rubber, no thorough treatise on the entire science of rubber has been available. The translation of Memmler's book was prompted by the belief that American and British rubber scientists and technologists would welcome a really comprehensive work in English covering not only latex, crude rubber, the chemistry of rubber, vulcanization, and the analysis of rubber, but also such diverse fields as microscopy and pigment dispersion, the physics of rubber, and the recently developed, specialized equipment for physical testing.

Although the general arrangement of the translation is similar to that of the German edition, certain changes and additions have been made. Occasional obvious errors have been corrected. A great deal of time has been devoted to the checking and correction of references. In this connection, the translators gratefully acknowledge their indebtedness to Miss Isabelle Welch of the Chemical Catalog Company, who checked many of the less accessible references in the libraries of Washington and New York.

An earnest endeavor has also been made to supplement the original work with translators' notes covering the newer developments since the German text was written, and in a measure bringing the work up to date. Specific mention may be made of the translators' notes on recent developments in synthetic rubber, on the compounding and the direct utilization of latex, on gutta-percha (which was not discussed in the German version), on recent X-ray work, on the latest physical testing equipment (with emphasis on that of American origin), and on the recently developed theories of vulcanization. In addition the editors feel that the value of the book has been greatly increased by a comprehensive bibliography, in which an attempt has been made to include references to all important books and pamphlets on rubber. This bibliography was compiled by Miss H. P. Albaugh, Research Librarian of the Firestone Tire and Rubber Company.

The translators selected by the editors were in nearly every case those members of the Firestone Research Staff best qualified to translate the sections of the book apportioned to them.

The editors wish to acknowledge their indebtedness to the Firestone Tire and Rubber Company for providing library facilities and the necessary typing service. An expression of appreciation is due Dr. N. A. Shepard, Director of Research, who not only contributed to the translation but who also gave his whole-hearted support to the entire project from the moment of its inception. The editors are especially indebted to Miss Hilda P. Albaugh, Research Librarian, who reviewed the entire manuscript in the role of literary critic.

Notable assistance in connection with the translation or the editorial criticism was also rendered by Mr. E. B. Babcock, Mr. C. R. Park, Dr. N. Johnston, Mr. H. W. Greenup, Dr. O. D. Cole, Dr. C. S. Dewey, Dr. B. J. Humphrey, Mr. J. E. Whittenberg, and Dr. M. H. Zimmermann. Finally, the translators wish to thank Messrs. G. S. Haslam and F. A. Steele of the New Jersey Zinc Company for criticizing the chapter on microscopy, Dr. E. C. Stakman of the University of Minnesota, and Dr. Paul Acquarone of the University of Akron for reviewing parts of the sections on botany and on plant physiology, and Dr. R. H. Ulrich, of the Firestone Development Department, who willingly placed at their disposal his thorough knowledge of the German language.

V. N. MORRIS.
R. F. DUNBROOK.

October, 1934

Preface

In 1910, Prof. Dr. W. Hinrichsen and the writer published the book, "Der Kautschuk und seine Prüfung." At the suggestion of the late Geh.-Rat Prof. Martens, who at that time was the Director of the Materialprüfungsamt, we were engaged in developing for the Bureau, chemical and mechanical tests for soft rubber products. In this undertaking, we were assisted by our collaborators, Kindscher and Schob. The large amount of fundamental experimental work then performed, especially the mechanical testing, is fully described in the reports of the Materialprüfungsamt for the years from 1909 to 1913 inclusive. "Der Kautschuk und seine Prüfung" represented the first attempt to gather these newly revealed facts into book form. It was well received both here and abroad, especially because there were so few contemporary books on the subject. A second edition would have been issued had not the World War intervened. This event decided the further fate of the book, as it demanded the sacrifice of my co-worker, Hinrichsen, who had been especially devoted to his investigations in the chemistry of rubber. He died a hero's death on Russian soil. All honor to his memory!

It was my good fortune to be able to fill an important position in the army service by assisting in the solution of the problem of the war-time rubber emergency in Germany. While this was a laborious and responsible activity, it brought me greatly enriched experience in the field of rubber. Immediately after the end of the war, the publishers approached me regarding a new edition of the book. Because of various duties and personal reasons, I could not bring myself to undertake the task at that time. The subject covered by the book was in such a state of flux that it did not seem to be the proper time to issue a new edition having the restricted scope of the previous work. The idea of undertaking a comprehensive review of the entire field of rubber science was gradually evolved. Because of the vigorous research activities along all branches of rubber science in practically all civilized countries, it seemed wise to delay this project until a more appropriate time. Since the knowledge in this field had become so extensively developed, it was obvious that the production of such a work would be practical only if it were the combined effort of several men. A number of authorities could discuss their respective fields so thoroughly that the whole would be a very desirable addition to the German literature on rubber.

Fortunately, I have had the assistance of such a group of well-known technical men, and it is a privilege to be able to thank them here for so unselfishly contributing their rich store of specialized knowledge. I am now able to submit the completed work to the public not as a second, enlarged edition of the earlier book, but as the first edition of a new publication.

There are sure to be varying opinions as to whether this is the proper time for the presentation of such a book. Certainly rubber as a scientific problem with chemical, physical, and technical aspects, is receiving diligent attention such as is being accorded few other fields of investigation. This is demon-

strated by the fruitful contributions of the young Deutschen Kautschuk-Gesellschaft. Moreover, the many investigators interested in this problem have so greatly expanded the special literature in the technical journals that a survey by any one individual becomes increasingly difficult. Therefore, my collaborators and I have agreed to risk presenting to the public the result of six years' work. We fully realize that the results of subsequent researches are certain to supplement or change much that is contained herein. Our efforts will not have been in vain, however, if this review serves to facilitate future work.

In regard to the scope of the contents, I was of the opinion that the technology of the preparation of rubber goods and factory practice should be omitted from a book which was devoted for the most part to the more fundamentally scientific aspects of rubber. Several new books pertaining to factory practice had appeared, notably those of Kirchhof and Gottlob. Furthermore, it seemed to me that a pure scientist should not publish his knowledge of the applied science if it be incomplete or out of date. Only an expert who has been in constant contact with factory practice possesses a real understanding of the present processes of manufacturing rubber goods. The experience of such an individual does not usually equip him for participation in a work of this kind, for with rare exceptions, he is completely familiar with but one phase of technology. The same situation exists to a large extent in the field of reclaiming. For this reason, merely the theoretical side of the problem of reclaiming is presented, with only a brief description of the basic principles of the best-known reclaiming processes.

In the remaining sections of this treatise, the authors have tried, for the sake of completeness, to offer explanations and critical discussions of pertinent and worthy publications, in addition to the presentation of their own special researches. Information is thus provided for those with only a general interest in rubber, as well as for specialists in the fields of botany, planting, chemistry, physics, and the testing of materials. We shall be very grateful for criticisms as to omissions or errors, and shall gladly consider those of merit for future editions.

In closing, I join with my co-workers in thanking the publisher, S. Hirzel, who has spared no effort to assist us in this work, and to confer upon the book a worthy appearance with respect to printing and style.

I must also express my hearty thanks to Prof. Dr. E. Hauser, who kindly placed at my disposal, for the first part of the book, nine photographs from his Indian films. Acknowledgment is also gratefully made to Verlag G. Fischer, Jena, and the Kolonialwirtschaftlichen Komitee of Berlin for the use of several cuts, as well as to the Continental Caoutchouc- u. Guttapercha-Compagnie of Hanover, for preparing valuable illustrative material for the chapter on microscopy.

K. MEMMLER.

Berlin-Dahlem,
January, 1930.

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List of Abbreviations

Abbreviation	Complete Title
Agr. Bull. Federated Malay States	Agricultural Bulletin of the Federated Malay States
Agr. Bull. Str. Federated Malay States	Agricultural Bulletin of the Straits and Federated Malay States (1902-1911)
L'Agr. prat.	L'Agriculture pratique des Pays Chauds
Agr. J. India	Agricultural Journal of India
Am. J. Sci.	American Journal of Science
Am. J. Roentgenol. Radium Therapy	American Journal of Roentgenology and Radium Therapy
Amtsblatt f. d. Schutzgebiet, Togo.	Amstblatt für das Schutzgebiet, Togo
Analyst	The Analyst
Ann. acad. sci. Toulouse	Annales de l'academie des sciences de Toulouse
Ann. de l'Inst. Bot. de Btzorg.	Annales de l'Institut botanique de Buitenzorg, Java
Ann. Botany	Annals of Botany
Ann. chim.	Annales de chimie
Annales de la Faculte des sciences de Toulouse	Annales de la Faculte des sciences de Toulouse (see Ann. acad. sci. Toulouse)
Ann. chim. phys.	Annales de chimie et de physique
Ann. di Botanica	Annali di Botanica
Ann. jard. bot. Buitenzorg	Annales du jardin botanique de Buitenzorg
Ann. Physik	Annalen der Physik (1799-1818 and 1900-)
Ann. phys.	Annales de physique
Annual Repts. Appl. Chem.	Annual Reports of Applied Chemistry
Arch. Rubbercultuur	Archief voor de Rubbercultuur in Nederlandsch-Indië
Arch. Zellforsch.	Archiv für Zellforschung
Atti. accad. Lincei	Atti della reale accademia dei nazionale dei Lincei. Rendiconti
Ber. deut. botan. Ges.	Berichte der deutschen botanischen Gesellschaft
Ber.	Berichte der deutschen chemischen Gesellschaft
Ber. deut. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft
Ber. deut. physik. Ges.	Berichte der deutschen physikalischen Gesellschaft
Ber. preuss. akad. Wiss.	Sitzungsberichte der preussischen akademie der Wissenschaften, Berlin
Biochem. J.	Biochemical Journal
Bot. Archiv.	Botanisches Archiv, Zeitschrift für die gesamte Botanik
Botan. Jahrb.	Botanische Jahrbücher
Botan. Mag.	The Botanical Magazine, Tokio
Botan. Ztg.	Botanische Zeitung
Braunkohle	Braunkohle
Brit. Pat.	British Patent
Bull. Dept. Landbouw Suriname	Bulletin van het Departement van den Landbouw in Suriname (Paramaribo)
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan
Bull. Dept. Agr. Ceylon	Bulletin of the Department of Agriculture, Ceylon

Abbreviations	Complete Title
Bull. Imp. Inst.	Bulletin of the Imperial Institute
Bull. caoutchoucs inst. colonial Marseille.	Bulletin des caoutchoucs de l'institut colonial de Marseille
Bull. jard. bot. Buitenzorg	Bulletin du jardin botanique de Buitenzorg
Bull. Musée Ind. Belg.	Bulletin du Musée de l'Industrie de Belgique
Bull. Rubber Growers' Assoc.	Bulletin of the Rubber Growers' Association
Bull. Rubber Res. Scheme Ceylon	Bulletin Rubber Research Scheme, Ceylon
Bull. soc. chim.	Bulletin de la société chimique de France
Bur. Standards	Bureau of Standards
Bur. Standards, Circ.	Bureau of Standards, Circular
Bur. Standards J. Research	Bureau of Standards Journal of Research
Bur. Standards Sci. Paper	Bureau of Standards Scientific Paper
Bur. Standards Technol. Paper	Bureau of Standards Technological Paper
Caoutchouc & gutta-percha	Le caoutchouc & la gutta-percha
Chem. Abstracts	Chemical Abstracts
Chem. Age	Chemical Age
Chem. & Met. Eng.	Chemical & Metallurgical Engineering
Can. J. Research	Canadian Journal of Research
Chem. News	Chemical News
Chem. Rev.	Chemical Reviews
Chem. Trade J.	The Chemical Trade Journal and Chemical Engineer
Chem. Zentr.	Chemisches Zentralblatt
Chem.-Ztg.	Chemiker-Zeitung
Chem. Weekblad	Chemisch Weekblad
Chimie & industrie	Chimie & industrie
Compt. rend.	Comptes rendus hebdomadaires des séances de l'académie des sciences
Cultuur gids	Cultuur gids, 1-8, 1899-1911
Dept. Agr. Federated Malay States Bull.	Department of Agriculture, Federated Malay States, Bulletin
Dept. of Commerce, Trade Promotion Series	Department of Commerce, Bureau of Foreign and Domestic Commerce, Trade Promotion Series
Dep. Landb. Nijverh. en Handel, Mededeel. over Rubber	Department van Landbouw, Nijverheid en Handel, Mededeelingen over Rubber, 1911-1915
Delft Comm.	Communications of the Netherlands Gouvernement Institute for advising the Rubber Trade and the Rubber Industry
Deut. Kolonialblätter	Deutsche Kolonialblätter
Deut. Luftfahrer-Ztg.	Deutsche Luftfahrer-Zeitung
Dept. Agr. Ceylon Bull.	Department of Agriculture, Ceylon, Bulletin
Elek. Z.	Elektrische Zeitschrift
Eng. Mining J.	Engineering and Mining Journal
Ergeb. exakt. Naturwissen.	Ergebnisse der exakten Naturwissenschaften
"Estate Rubber"	O. de Vries, "Estate Rubber, Its Preparation, Properties and Testing," Ruygrok & Co., Batavia, 1920
Farben-Ztg.	Farben-Zeitung
Flora	Flora (Allgemeine Botanische Zeitung)
Fortschr. Physik	Fortschritte der Physik
Fortschr. Chem. Physik physik. Chem.	Fortschritte der Chemie, Physik und physikalischen Chemie
French Pat.	French Patent
Friedländer, "Fortschritte"	P. Friedländer, "Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige"

ABBREVIATIONS	COMPLETE TITLE
azz. chim. ital.	Gazzetta chimica italiana
Ger. Pat.	German Patent (D. R. P.)
Giorn. chim. ind. applicata	Giornale di chimica industriale ed applicata
Gummi-Ztg.	Gummi-Zeitung
Hawaii Agr. Exp. Sta. Bull.	Hawaii Agricultural Experiment Station Bulletin
Helv. Chim. Acta	Helvetica Chimica Acta
India Cultures	India Cultures
Indian J. Physics	Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science
India Rubber J.	India Rubber Journal
India Rubber World	India Rubber World
Ind. Eng. Chem.	Industrial and Engineering Chemistry
Ind. Eng. Chem. Anal. Ed.	Industrial and Engineering Chemistry, Analytical Edition
Ind. Merc.	De Indische Mercuur
Indian J. Physics	Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science
Inst. Rubber Ind. Trans.	Institute of the Rubber Industry, Transactions
Italian Pat.	Italian Patent
Jahresber. Fortschr. Chemie	Jahresbericht über die Fortschritte der Chemie und verwandter Teile anderer Wissenschaften (1847-1921)
Jahrb. wiss. Botan.	Jahrbuch für wissenschaftliche Botanik
J. Am. Chem. Soc.	Journal of the American Chemical Society
J. d'Agric. Trop.	Journal d'Agriculture Tropicale (Paris)
J. Biol. Chem.	Journal of Biological Chemistry
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan
J. Chem. Ind. Moscow	Journal of Chemical Industry (Moscow)
J. Chem. Soc.	Journal of the Chemical Society (London)
J. Franklin Inst.	Journal of the Franklin Institute
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry
J. Inst. Elec. Engrs. London	The Journal of the Institution of Electrical Engineers (London)
J. Linnean Soc.	Journal of the Linnean Society of New South Wales
J. Optical Soc. Am.	Journal of the Optical Society of America
J. phys. radium J. phys.	Le Journal de physique et le radium
J. Phys. Chem.	Journal of Physical Chemistry
J. prakt. Chem.	Journal für praktische Chemie
J. Rheol.	Journal of Rheology
J. Roy. Inst.	Journal of the Royal Institution of Great Britain
J. Roy. Microscop. Soc.	Journal of the Royal Microscopical Society
J. Rubber Soc. Japan	Journal of the Rubber Society, Japan (Gomei)
J. Russ. Phys. Chem. Soc.	Journal of the Russian Physical Chemical Society
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry (London)
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry (Japan)
J. Soc. Dyers & Colorists	Journal of the Society of Dyers & Colorists
J. tech. ökonom. Chem.	Journal für technische und ökonomische Chemie. Erdmann 1-18 (1828-1833)
Kautschuk	Kautschuk
Kolloidchem. Beihefte	Kolloidchemische Beihefte

Abbreviations	Complete Title
Kolloid-Z.	Kolloid-Zeitschrift
Kolonialw. Kom.	Kolonialwirtschaftliches Komitee
Koninklijke Akad. Wetenschappen Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam
Kunststoffe	Kunststoffe
Landw. Jahrb.	Landwirtschaftliche Jahrbücher
Lect. India Rubber	"Lectures on India Rubber," edited by D. Spence, 1909
Leipzig. Ber.	Leipziger Berichte
Malayan Agr. J.	Malayan Agricultural Journal, The
Mededeel. Algem. Proefsta. A. V. R. O. S.	Mededeelingen van het Algemeen Proefstation der Algemeene Vereeniging van Rubberplanters ter Oostkust van Sumatra
Mededeel. Algem. Proefsta. Landbouw.	Mededeelingen van het Algemeen Proefstation voor den Landbouw van het Departement van Landbouw, Nijverheid en Handel
Mededeel. Besoekisch. Proefsta. Rubberserie.	Mededeelingen van het Besoekisch Proefstation Rubberserie
Mededeel. Agr. Chem. Buitenzorg	Mededeelingen van het Agricultuur Chemisch Laboratorium Buitenzorg
Mededeel. Centraal Rubbersta.	Mededeelingen van het Centraal Rubberstation. Buitenzorg, Java
Mededeel. Rubberproefsta. West Java	Mededeelingen van het Rubberproefstation West Java
Mededeel. over Rubber	Mededeelingen over Rubber (issued in Dutch by the Department of Agriculture) Buitenzorg, Java
Mededeel. Proefsta. Malang	Mededeelingen van het Proefstation Malang
Mededeel. uit's Lands Plantentuin	Mededeelingen uit's Lands Plantentuin. Buitenzorg, Java
M. P. A.	Staatliches Materialprüfungsamt zu Berlin-Dahlem
Medizin. Jahrbuch.	Medizinische Jahrbücher
Mem. Lit. Phil. Soc. Manchester	Memoirs of the Literary and Philosophical Society of Manchester
Mineralog. Mag.	The Mineralogical Magazine and Journal of the Mineralogical Society
Mitt. Materialprüfungsamt Berlin-Dahlem	Mitteilungen aus dem Staatlichen Materialprüfungsamt zu Berlin-Dahlem
Mitt. tech. Gewerbemus. Wien.	Mitteilungen des technologischen Gewerbemuseums in Wien
Nature	Nature
Naturwissenschaften	Naturwissenschaften
Nuovo cimento	Il nuovo cimento
Notiz-Bl. Bot. Gart. u. Mus. Berlin App.	Notizblatt Botanischer Garten und Museum, Berlin
Pflanzer	Pflanzer
Pharm. Ztg.	Pharmazeutische Zeitung
Phil. Mag.	*Philosophical Magazine*
Phys. Rev.	Physical Review
Physics	Physics
Physik. Ber.	Physikalische Berichte
Physik. Z.	Physikalische Zeitschrift

ABBREVIATIONS	COMPLETE TITLE
g. Ann.	Poggendorf's Annalen der Physik und Chemie (1824-1877)
Proc. Am. Soc. Testing Materials	Proceedings of the American Society for Testing Materials
Proc. Chem. Soc.	Proceedings of the Chemical Society (London)
Proc. Phys. Soc. London	The Proceedings of the Physical Society (London)
Proc. Roy. Soc. London	Proceedings of the Royal Society (London)
Proc. Tokyo Math. Phys. Soc.	Proceedings of the Tokyo Mathematico-Physical Society
Proc. Phys. Math. Soc. Japan	Proceedings of the Physico-Mathematical Society of Japan
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas
Rend. ist. lombardo sci.	Rendiconti reale istituto lombardo di scienzi e lettere
Rend. di Napoli	Rendiconti di Napoli
Rev. cult. coloniales	Revue des cultures coloniales
Rev. gén. caoutchouc	Revue générale du caoutchouc
Roy. Botan. Gard. Ceylon, Circ.	Royal Botanic Gardens Ceylon, Circulars
Roy. Botan. Gard. Kew Bull.	Royal Botanic Gardens Kew Bulletins and miscellaneous information
Rubber Age (N. Y.)	Rubber Age (New York)
Rubber Age (London)	Rubber Age (London)
Rubber Chem. Tech.	Rubber Chemistry and Technology
Rubber Recueil	International Rubber Congress, Batavia, 1914, Rubber Recueil (De Bussy, Amsterdam)
Rubber Res. Scheme Bull.	Rubber Research Scheme (Ceylon) Bulletin
Science Repts. Tohôku Imp. Univ.	The Science Reports of the Tohôku Imperial University
Sitzber. preuss. Akad. Wiss.	Sitzungsberichte der preussischen Akademie der Wissenschaften
Sitzber. Akad. Wiss. Wien.	Sitzungsberichte der Akademie der Wissenschaften in Wien
Teysmannia	Teysmannia (Buitenzorg)
Trans. Am. Electrochem. Soc.	Transactions of the American Electrochemical Society
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Am. Inst. Elec. Engrs.	Transactions of the American Institute of Electrical Engineers
Trans. Inst. Rubber Ind.	Transactions of the Institution of the Rubber Industry
Trans. Roy. Soc. Can.	Transactions of the Royal Society of Canada
Trans. Roy. Soc. London	Transactions of the Royal Society (London), Philosophical
Tropenpflanzer	Der Tropenpflanzer
Tropenpflanzer Beihefte	Der Tropenpflanzer Beihefte
Trop. Agr.	The Tropical Agriculturist
"Untersuchungen . . ."	C. Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten," J. Springer, Berlin, 1919
U. S. Dept. Agr. Bur. Plant Ind. Bull.	United States Department of Agriculture, Bureau of Plant Industry, Bulletins
U. S. Pat.	United States Patent
U. S. Nat. Herbarium	United States National Herbarium
Verhandl. d. Botan. Vereins d. Provinz Brandenburg	Verhandlungen des Botanischen Vereins der Provinz Brandenburg

Abbreviations	Complete Title
Verhandel. Akad. Wetenschappen Amsterdam	Verhandelingen der koninklijke Akademie van Wetenschappen te Amsterdam
V. D. E. Vorschr.	Vorschriftenbuch des Verbandes deutscher Elektrotechniker
Verslag. Mededeel. Afdeel. Handel Dept. Landbouw.	Verslagenen Mededeelingen van de Afdeeling Handel van het Departement van Landbouw, Nijverheid en Handel
Wied. Ann.	Wiedemann's Annalen der Physik und Chemie (1877-1899)
Wiss. Veröffentlich. Siemens-Konzern	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern
Z. anal. Chem.	Zeitschrift für analytische Chemie
Z. angew. Chem.	Zeitschrift für angewandte Chemie
Z. anorg. allgem. Chem.	Zeitschrift für anorganische und allgemeine Chemie
Z. Biol.	Zeitschrift für Biologie
Z. Chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide
Z. Elektrochem.	Zeitschrift für Elektrochemie
Z. Physik	Zeitschrift für Physik
Z. physik. Chem.	Zeitschrift für physikalische Chemie
Z. Krist.	Zeitschrift für Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie
Z. tech. Physik	Zeitschrift für technische Physik
Z. wiss. Mikroskop.	Zeitschrift für wissenschaftliche Mikroskopie und für mikroskopische Technik
Zentr. Bakt. Parasitenk. Abt. II	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten, Abteilung II

SCIENCE OF RUBBER

Introduction †*

History of Crude Rubber

The natives of localities where rubber trees grew seem to have been familiar with rubber long before its existence was first recorded in history. Excavations conducted by Gann[1] in British Honduras have revealed a Mayan civilization dating back to at least the eleventh century. These excavations disclosed the remains of a ball-ground, or court, which had been used by the Maya Indians in playing their favorite game. The game consisted in hurling, with the shoulder or hip, a rubber ball about the size of the modern football through a stone ring fixed vertically to a wall. The diameter of the ring was only slightly greater than that of the ball. Among other discoveries in the vicinity of the playing-field was a temple dedicated to the rain god, where sacrificial gifts had been sunk in a sacred well. These offerings were balls of rubber.

Rubber was first mentioned in the writings of Pietro Martyre d'Anghiera,[2] Salahan,[3] and Gonzalo Fernandez de Oviedo y Valdez[4] wherein it is recorded that elastic balls were used by the Indians in playing games. Antonio de Herrera Tordesilla[5] also mentions rubber in his work concerning the wanderings and conquests of the Castilians. According to this source, Columbus, on his second voyage to America (1493-1496) learned of a game played by the natives of Haiti in which balls of an "elastic tree-resin" were used. In 1615, Juan de Torquemada[6] described the preparation of a substance called "ulei," which was obtained by the natives of Mexico from a tree known as the "Ulequahuil" or "Ule" *(Castilloa elastica)*. The Indians ascribed great healing properties to this substance, and also employed it to waterproof garments.

The first record of scientific importance was written by Charles Marie de la Condamine, who, by commission of the Academy of Science of Paris, undertook a voyage to Ecuador in 1735 with Bougeur and Godin, to survey a parallel of latitude below the equator. The expedition left La Rochelle May 16, 1735, and arrived in Guayaquil, May 13, 1736. From Guayaquil, the route led to Quito by difficult overland trails. Here, in the midst of the double ranges of the Andes, the laborious measurements were taken. During this journey, which lasted more than eight years, many observations regarding the natural science of the region were recorded. La Condamine sent various specimens from Quito to the Academy in Paris, among which were some pieces of a dark, resinous mass, whose origin he describes as follows:[7]

"There grows in the province of Esmerelda, a tree which the natives call 'heve'. When the bark is cut, a white, milky fluid runs out and gradually

† Translated by J. E. Whittenberg.

* The editor is especially indebted to E. Kindscher for the collection of historical and statistical data.

[1] See F. C. Jones, *India Rubber J.*, **66**, 219, 328 (1923); F. M. Feldhaus, *Gummi-Ztg.*, **41**, 551 (1926).
Translator's Note: See also *Rubber Age* (London), **4**, 391 (1923); **5**, 501 (1924).

[2] "De orbo nuovo," **1521.**

[3] "A General History of the Products of New Spain," **1529.**

[4] "Historia general y natural de las Indas," vol. **5**, II, 165; Seville, **1535**; Madrid, **1851.**

[5] "Historia general de los hechos de los Castellanos en las islas y tierra firme del mar oceano 1492-1554," Madrid, **1601-1615**; Antwerp, **1728.**

[6] "De la monarquia indiana," Vol. II, Chapt. 43, p. 663, Madrid, **1615.**

[7] Histoire de l'académie royale des sciences, **1751**, page 17; Memoires de l'académie royale des sciences, **1751**, page 314.

solidifies and darkens in the air. The people make torches of this resin. In the province of Quito, cloth is coated with it and is thus made waterproof. The same tree grows on the banks of the Amazon River, where the substance obtained from it is called 'cahutchu'.[8]

"The natives prepare water-tight shoes of one piece from this material. They also spread it over an earthen, flask-like form, and when the fluid has solidified, they break up the earthen form, remove the fragments through the neck of the bottle, and thus obtain a light, unbreakable vessel suitable for holding liquids."

In the later writings of La Condamine are found the reports of the French investigator, Francois Fresneau, who at that time was living in Guiana, and whom La Condamine met in 1743. Although La Condamine was the first to send news of rubber to Europe, it seems that Fresneau[9] was the first to have seen the rubber tree itself and to have witnessed the method of obtaining rubber. A complete description of the tree called "seringue" by the Portuguese of Para and "heve" by the Maina Indians occurs in his reports concerning the plant life of Guiana. He also reported the location of the trees and the method of obtaining the rubber. This information was obtained through his own untiring efforts. Fresneau also offered the first suggestions for the practical application of this material. He thought that divers' apparel, hose, and air-tight bags could be made from fabric impregnated with rubber, and that the bags could be used for preserving food while traveling. He later proved the feasibility of his ideas by making various articles out of latex and sending them to the French minister, Maurepas.

It was in 1762 that the French botanist, Jean Baptiste Aublet[10] gave the name *"hevea guyanensis"* to the tree described by Fresneau. His countryman, M. Coffigny, succeeded in 1765 in obtaining the same "resin" from a different kind of plant in Madagascar. J. Howison first discovered (1798) a rubber-yielding vine *(Urceola elastica)* in Penang, Straits Settlements. Soon after, W. Roxburg found other rubber trees *(Ficus elastica)* in Assam. In his "Flora indica"[11] Roxburg writes that the natives of eastern Asia knew of the uses of rubber, and had used it for a long time to make torches and to waterproof plaited baskets, jars, etc.

Beginnings of Technical Use*

When, through the accounts of travelers, the valuable properties and significant possibilities of rubber had become known in Europe, interest centered upon finding a way to use it commercially. Fresh latex was available to the natives of the rubber-producing districts, but only solid rubber could then be obtained in Europe. Therefore, a solvent was sought which would dissolve the solid rubber and which upon evaporation would yield a rubber of unchanged properties. Such a solvent would render the material capable of being worked into any desired form. The French chemists, Hérissant and Macquer, proposed the use of oil of turpentine or ether, especially the latter, as a method

[8] From this name, which, according to W. H. Johnson, comes from "caa" (tree) and "o-chu" (to weep) originated the name "caoutchouc." Hence the German "Kautschuk," the French "caoutchouc," the Italian "cauccio," and the Spanish "caucho" or "cauchuc." The English equivalent, "India rubber" and the Portuguese "borracha" (tube) are exceptions. The German word "Gummi" arose from the erroneous conception of rubber as a vegetable gum (*"gummi elasticum"* corresponding to *"gummi arabicum"*).

[9] See J. Ch. Bongrand, *Rev. gén. caoutchouc*, I, **3**, 43, 442; **5**, 34; **6**, 48; **7**, 43 (1924). Translator's note: Cf. also *India Rubber J.*, **82**, 857 (1931).

[10] "Histoire des plantes de la Guiane française," p. 174 Paris, **1775.**

[11] Volume 3, page 472.

* Translator's Note. For additional information concerning the early technical history of rubber, see *India Rubber J.*, **82**, 857 (1931).

for solving this problem (1761). Macquer employed ether in the production of elastic tubes (1768) by the following method:

A wax cylinder was coated with an ether solution of rubber. After evaporation of the solvent, the rubber remained upon the surface of the cylinder as a thin, continuous film. By frequent repetition of this process, a layer of any desired thickness could be obtained. The wax was then melted by placing the cylinder in hot water. Thus were prepared rubber tubes which were the forerunners of modern rubber tubing.

In 1770, the famous English chemist, Priestley, reported that rubber was especially suitable for the cleaning of soiled paper.* He pointed out particularly its remarkable property of removing lead pencil marks from paper without noticeably harming the surface. Magellan (1772) brought small cubes of rubber into the French market for this purpose, and soon the rubber eraser became generally known. To this method of use, rubber owes its English name, "India rubber" ("India" from "West Indies").

Although Hérissant and Macquer had developed practical methods of manufacture, no commercial application of these methods had been made up to the year 1791. In this year, Samuel Peal[12] patented a process involving the use of rubber in turpentine solution, or in the form of latex, for the preparation of waterproof gummed fabric. His patent also covered the impregnation of leather, yarn, woolen goods, silk, paper, wood, etc., as well as the preparation of flasks, shoes, and other articles from rubber. The state of knowledge at that time concerning rubber is revealed by a very interesting article written by the English physician, J. Anderson,[13] which appeared in the "Bee or Literary Weekly Intelligencer" under the title "On the Uses that may be made of Caoutchouc, Elastic Gum, or Indian Rubber in Arts and Manufacture, with an Account of the Manner of Obtaining and Manufacturing It."

Charles Macintosh established in Glasgow in 1823 the first factory for the manufacture of rubber goods. Waterproof fabrics were made there by a patented process, using a benzene solution of rubber. The rubber coating obtained was covered with a second layer of fabric. This product soon became generally known by the name, "macintosh," a familiar name even today. Later, this first industrial establishment was transferred to a location near Manchester, where it is now an important producer of rubber goods.

A distinct advance in the industry was accomplished through the work of Thomas Hancock.[14] He was first interested (1824) in the coating of fabric by the use of solutions of rubber and in the use of latex, small quantities of which had arrived in Europe in good condition. In 1830, he bought latex through an agent in Tampico, and had it shipped in air-tight, sealed containers. In most cases, however, these shipments arrived in Europe in a coagulated condition. Therefore, the idea of the direct use of latex was abandoned. Although these early experiments were very interesting in themselves, Hancock's later work proved to be much more important in the further development of the utilization of rubber.

In 1826, he noticed that freshly cut pieces of rubber would stick together

* Translator's Note. The idea of using rubber as an eraser appears to have originated with Nairne, a maker of mathematical instruments in London. Cf. *Gummi-Ztg.*, **43,** 2270 (1929).

[12] Brit. Pat. 1801 (1791). Translator's Note. A description of early patents in the rubber industry is given by H. K. Turner, *India Rubber J.*, **82,** 827 (1931).

[13] Edinburgh, March 23, 1791; *India Rubber J.*, **68,** 265 (1924).

[14] Thomas Hancock, "Personal Narrative of the Origin and Progress of the Caoutchouc or India Rubber Manufacture in England." London, **1857**; new edition, **1920.** Brit. Pat. 5024 (1824); 5122 (1825); 5970 (1830).

if pressed. By pressing together bits of rubber, and by cutting sections from the resulting slabs, he hoped to prepare blocks of any desired size and form, and thus to become independent of the dimensions of the imported bales in the manufacture of the desired rubber articles. With this aim in view, he constructed a "tearing machine" or "pickle," having a roll supplied with prongs and rotating in a jacket fitted likewise. However, rubber was not comminuted as expected in this machine. Instead, under the influence of the heat generated, it came out in the form of a plastic, coherent, and homogeneous mass. The same result was obtained when the rubber was introduced in the form of little pieces. Hancock later improved this device by inner heating, and called it a "masticator." From the plastic raw rubber, he was able to form blocks of any desired size by the use of pressure. By means of another machine, he could then cut slabs of various thicknesses from these blocks. Although the form and dimensions of the "masticator" have been changed in the past century, the construction of the modern devices which form the foundation for practically all rubber processing is based upon the principles used by Hancock.

In 1828, Johann Nepomuk Reithofer took out a patent in Vienna covering a process whereby rubber threads, cut from Para rubber, were woven with linen, silk, or woolen threads. A similar process led in 1829 to the founding of the first German factory for the production of elastic fabric—the establishment of François Fonrobert in Finsterwalde near Berlin.

The rubber articles produced by the processes just described were all characterized by a disagreeable odor, as well as by a marked sensitivity to heat and cold. When cold, they were stiff, and when warm, they were sticky. In 1832, the German chemist, F. Lüdersdorff[15] found that rubber which had been dissolved in turpentine and then heated with sulfur, lost its stickiness after evaporation, and exhibited greater stability. Similar observations were made soon after by van Guens in Holland and by Nathaniel Hayward in America. Although these workers did not seem to realize the significance of their discoveries, and did not attach any practical value to them, they were the first to employ sulfur in the working of rubber.

In America, the technician Charles Goodyear[16] had, since 1831, been busily occupied with experiments directed toward the improvement of the properties of rubber. In particular, he hoped, by mixing powdered substances with rubber, to eliminate the undesirable stickiness of the surface. His early experiments resulted in repeated failures. Finally he became acquainted with Nathaniel Hayward, who, as was mentioned above, had already used sulfur in experiments with rubber. Goodyear and Hayward[17] took out a patent on a mixture of rubber and sulfur. Articles formed from such a mixture were exposed to sunlight for some time, whereby they lost their tackiness. In 1839, Goodyear observed that rubber, reacting with sulfur at higher temperatures (i. e., above the melting point of sulfur), and especially in the presence of lead compounds, gave a product distinctly superior to the raw material both in mechanical properties and in resistance to change of temperature.[18]

Goodyear did not patent his discovery at first. In 1842, a vulcanizate of this kind came into the hands of Thomas Hancock, and in the following year,

[15] *J. tech. ökonom. Chem.*, **15**, 353 (1832). Translator's Note: Cf. also *Gummi-Ztg.*, **46**, 967 (1932).

[16] Born December 29, 1800, in New Haven, Conn.; died July 1, 1860, in New York.

[17] Charles Goodyear, "Gum Elastic," vol. I, p. 112, New Haven, Conn., **1855**.

[18] According to W. Jorissen, *Chem. Weekblad*, **11**, 852 (1914); **12**, 801 (1915); **16**, 527, 1014 (1919), Jan van Guens, an apothecary living in Harlem, was supposed to have vulcanized rubber before 1836. For the story of vulcanization, see John Hancock Nunn, *India Rubber J.*, **59**, 936 (1920).

he was able to identify sulfur and rubber as the principal ingredients of the mixture. He could not, however, find a way to prepare such a vulcanizate. Numerous experiments having as their object the transformation of rubber into its new "modification" reached their climax November 21, 1843, in a patent issued to Hancock,[19] according to which "vulcanization" was effected by lengthy immersion of rubber in a bath of molten sulfur, or by heating rubber or its mixtures[20] with other materials, together with sulfur, in a high-pressure steam autoclave. The designation of the process as "vulcanization" originated with Brockedon, who discussed with Hancock the necessity of giving the new process a trade name. To Hancock we also owe the observation that if rubber strips remained in the sulfur bath for a longer time than was required for the formation of soft vulcanized rubber, they became dark and horny, forming "ebonite" or "hard rubber."*

When Goodyear found that his secret had been discovered, he had his process protected in 1844 by patents in America and England.[21] According to the terms of his patents, mixtures of rubber, sulfur, and white lead were heated (dry) at atmospheric pressure and suitable temperatures.

In 1845, Keene also succeeded in effecting vulcanization by treating rubber with sulfur vapor; but neither this process nor the Hancock sulfur-bath method attained in the future the importance of "hot vulcanization," i. e., the heating of rubber-sulfur mixtures at temperatures above the melting point of sulfur.

Alexander Parkes[22] found, in 1846, that the improvements in the quality of raw rubber were attained not only by heating with sulfur, but also by immersing the formed raw material for a short time at room temperature in a solution of sulfur monochloride in carbon disulfide ("cold vulcanization"). However, this process, as well as the one discovered in 1878 by Abbott[23] for the vulcanization of formed rubber articles in sulfur monochloride vapor, could only be used for the preparation of thin-walled articles, while hot vulcanization could be applied to the manufacture of articles with walls of any thickness.

A few years later, Nelson Goodyear, son of the discoverer of hot vulcanization, is supposed to have made an observation which was also to become of importance in the art. Hancock had already established the fact that by long treatment of rubber strips in a sulfur bath, hard rubber was produced. Nelson Goodyear succeeded, in 1851, in manufacturing the same product by heating mixtures of rubber with larger amounts of sulfur than were necessary for the production of elastic "soft rubber." In the same year, he produced in the "Crystal Palace" exhibit a room consisting in all its furnishings of ebonite.[24]

Improvement of the properties of raw rubber was at last accomplished after much difficulty; but it was found later that the natives of Brazil had long known of a process similar to vulcanization. Henry C. Pearson[25] reported in his book, "The Rubber Country of the Amazon," that, since early times, the Indian tribes had stretched fabrics coated with latex upon frames and let them

[19] Brit. Pat. 9952 (1843).

[20] The mixtures were prepared in a "masticator."

* Translator's Note: The possibility that hard rubber had been accidentally prepared by Prof. Petter Jonas Bergius in Stockholm some time prior to 1791 is suggested by B. D. Porritt and H. Rogers, *India Rubber J.*, **68**, 274 (1924).

[21] Brit. Pat. 10027 (1844), granted to W. E. Newton. Translator's Note. The specification of Goodyear's U. S. Pat. 3,633 of June 15, 1844, is reproduced in an article by J. Rossman in *India Rubber World*, **86**, No. 1, 48 (1932).

[22] Brit. Pat. 11146 (1846).

[23] Brit. Pat. 166 (1878).

[24] *India Rubber World*, **47**, 20 (1912).

[25] New York, **1911**; see also E. A. Hauser, "Latex," p. 6, Verlag von Theodor Steinkopff, Dresden and Leipzig, **1927**; English translation by W. J. Kelly, p. 11, Chemical Catalog Co., New York, **1930**.

dry in the sun. The latex used was mixed with sulfur or gunpowder. In one of these fabrics originating in South America, H. P. Stevens was able to determine the presence of 1.57 per cent sulfur, of which 0.9 per cent was combined with the rubber.

Development of Rubber Goods Manufacture in Germany [26]

The discovery of the various vulcanization processes greatly increased the possible uses of rubber, and soon resulted in the erection of factories for the production of rubber goods in practically all civilized countries. A factory for the manufacture of elastic fabric was built in 1829 in Finsterwalde near Berlin, and in 1849, the "Vereinigte Berlin-Frankfurter Gummiwarenfabriken" was established in Gross-Lichterfelde near Berlin by Elliot, an Englishman. The following year saw the beginning of the "Établissement Hutchinson," which was engaged in the manufacture of footwear. The first large hard rubber works was founded in 1856 as the "Harburger Gummikamm-Compagnie" (later known as "Dr. Heinr. Traun und Söhne"). In the same year, the "Harburger Gummiwerke Louis und Albert Cohen" was established. This company, which was known later as the "Vereinigte Gummiwarenfabriken Harburg-Wien," was making 10,000 pairs of rubber shoes daily in 1860, besides producing other soft rubber goods. Among other concerns founded at that time may be mentioned "Fonrobert und Pruckner" and "Voigt und Winde" in Berlin and "Ferd. Kohlstadt" in Cologne. The industry was started at Hanover with the establishment of the "Hannoversche Gummikamm-Compagnie" (later "Gummiwerke Excelsior") in 1862.

The rapid growth of the industry is shown by the fact that in 1868 there were thirty-six factories in the district of the North German Tariff Union producing articles from rubber and gutta-percha. These concerns were employing 1,788 workers at that time. The importance of this new industry was noted by G. v. Viebahn,[27] who wrote as follows:

"The imports coming through the tariff union in 1866 amounted to 29 tons of lacquered rubber goods, 18 tons of rubber-coated fabric, and 16 tons of rubber sheeting, as contrasted to exports of 311, 17, and 8 tons, respectively. This industry, in spite of its youth, has already acquired a considerable foreign market."

After the founding of the empire, German industry in general experienced a great development, which was aided by the favorable outcome of the war of 1870-71. The rubber goods industry expanded rapidly under these conditions, and in the ensuing years, many firms were founded. Among the first of these were the "Continental, Caoutchouc u. Gutta-Percha Co." in Hanover (1871), the "Mitteldeutsche Gummiwarenfabrik Louis Peter" in Frankfurt a.M. (1872), "Metzeler & Co." in Munich (1873), and the "Rhein. Gummi- und Celluloidfabrik" in Mannheim (1873).

A comprehensive perspective of conditions in the rubber industry in 1873 is given by the official catalog of the Vienna World's Fair, in which it is reported that the total production of rubber goods in Germany amounted to over 2,750 tons, of which 50 to 60 per cent was consumed at home. The consumption of the remainder, in the form of exports, was divided about equally between other European countries and foreign countries outside the continent. In 1875 there were in Germany 111 rubber factories, which em-

[26] Concerning the national and world-wide economic importance of the German rubber goods industry, see W. Vaas, "Die Kautschukwarenindustrie Deutschlands," Berlin, **1921.**

[27] "Statistik des zollvereinten und nördlichen Deutschlands," **3,** 1022 (1868). Berlin.

ployed 5,495 persons. In later years, the discovery of the pneumatic tire (1890) and the increased development of power vehicles (about 1895) and aircraft (about 1909), brought about in turn the manufacture of rubber goods on a still larger scale. The industrial census of the year 1895 listed 339 rubber factories steadily employing 12,514 persons, of whom 10,704 were employed in the 45 principal plants. In 1907, there were 539 plants giving employment to 31,909 workers. These figures steadily increased until in 1914 the number of factories exceeded 600, with about 45,000 workers.

The principal centers of the German rubber goods industry are: Berlin; Hanover; Hamburg-Harburg; the Rhine district with Cologne, Elberfeld, and Barmen; the middle and upper Rhine district with Frankfurt a.M., Offenbach, and Mannheim; Saxony, with Leipzig and Dresden; and Thuringia with Gotha, Waltershausen, and Erfurt.

The importance which the German rubber manufacturing industry had attained before the World War may best be judged by the fact that of the 108,440 tons of raw rubber which appeared on the world market in 1913, the following quantities were consumed in the respective countries:[28]

United States	48,000 tons
Great Britain	18,640 tons
Germany	15,500 tons
Russia	9,000 tons
France	6,500 tons

The remainder was divided among Belgium, Austria-Hungary, Italy, Scandinavia, Japan, and Australia. Although Germany stood in third place as a consumer of rubber, the supply of rubber goods for the world trade was, before 1914, dependent upon Germany. This was true in spite of the larger number of factories and larger production in the United States, because a large domestic market had to be satisfied in America. Thus the export of German rubber goods enjoyed a steady growth, and, as the following table will show, reached a position of considerable national economic importance.

Year	Tons	Value*
1890	3,811	$ 6,034,320
1895	4,167	5,460,480
1900	5,582	10,339,440
1905	8,736	14,962,800
1910	10,684	13,614,000
1911	12,019	14,970,000
1912	20,777	30,096,960
1913	22,559	32,403,360

With these exports valued at over 32 million dollars, Germany in 1913 was advancing to the first position among industrial countries. The principal buyers of German rubber goods at this time were England, France, Austria-Hungary, Italy, and Switzerland. The German rubber goods industry was in the lead not only with tires of all kinds, but also with electrical supplies, technical and surgical articles, sports goods, and hard rubber items. Although the German industry was in a position to cover fully the requirements of the home market for these articles, the importation of foreign rubber goods had increased steadily since 1895. In this field, Great Britain, Russia, the United States, France, Austria-Hungary, and Italy appeared as competitors of the German industry, and shipped in tires, technical goods, and reclaimed rubber.

[28] *Gummi-Ztg.*, **29**, 772 (1914).

* Translator's Note. These values were obtained by converting to dollars the original values given in marks (1 mark = 24 cents).

The quantity of these imports, however, amounted to only a third or a fourth of the quantity of rubber goods placed on foreign markets by the German firms. This was the state of things in 1914, at which time the picture suddenly changed.

The World War broke out, and the German rubber industry suffered severely, not only from the isolation which hampered the progress of the German people in the following years, but also from the post-war economic crisis. Foreign branches were lost; in countries which fought against Germany, they were liquidated; in other places, they had to be abandoned during the depression of values. For almost six years, export was impossible, with the result that Germany's former customers had to turn to other sources of supply. This opportunity was utilized especially by the United States, whose industries were able to develop freely during the war. The products of the American rubber goods industry were introduced into the markets in all parts of the world, and the United States assumed leadership in this trade. A survey of import and export statistics for the years 1926 and 1927 will show at a glance the position of the German rubber goods industry after the war.[29]

Germany imported 46,820 tons of crude rubber in 1927. Of this, 3,353 tons were again exported, giving a domestic consumption of crude rubber of 43,467 tons. This quantity is about two and one-half times the consumption of 1913, and indicates the greatly increased use of rubber goods. Table 1 shows the export of German rubber goods for these years:

TABLE 1.—*Export Statistics for the Years 1926 and 1927.*

	1926		1927	
	Tons	Value*	Tons	Value*
Soft rubber goods	16,924	$21,446,160	17,304	$22,247,760
Hard rubber goods	935	2,294,880	1,070	2,452,320
Total exports	17,859	$23,741,040	18,374	$24,700,080

Among the exports were reclaimed rubber, rubber solutions and unfinished goods, rubber thread, tubing, tires, driving belts, rubber shoes, sheet and cord packing, rubberized fabric, hard rubber articles, gaskets, and the like. As the figures in Table 1 show, the exports of rubber goods in 1927 were only slightly greater than those in 1926, and were much less in both quantity and value than in 1913.

Imports of rubber goods during the post-war period were much greater than in the pre-war period, and increased amazingly in 1926 and 1927. (*See* Table 2.)

TABLE 2.—*Import Statistics for the Years 1926 and 1927.*

	1926		1927	
	Tons	Value*	Tons	Value*
Soft rubber goods	3,719	$4,375,200	6,692	$8,922,240
Hard rubber goods	95	151,440	202	276,960
Total imports	3,814	$4,526,640	6,894	$9,199,200

It may be seen that in these years, the value of imports was doubled; as to amounts imported, the comparison is not so striking. The condition of a steadily increasing tendency toward import with an accompanying stagnation of export is not very pleasing. In any case, greater effort is needed if the former position of the German rubber goods industry is to be regained.

[29] *Gummi-Ztg.*, **42**, 1188 (1928).

* Translator's Note. These values were obtained by converting to dollars the original values given in marks (1 mark = 24 cents).

The Variety of Technical Fields of Application and Industrial Use of Rubber

Rubber has attained a position of great importance as a material of modern manufacture because of the diverse uses to which it may be put as a result of its peculiar physical and chemical properties. Since it is difficult to compile even an approximately complete list of the uses of rubber, the following paragraphs will mention only a few examples of the wide variety of materials manufactured from it.

Only a comparatively small amount of rubber in the unvulcanized state is applied to practical use. In the last decade, raw rubber has been used chiefly in the shoe industry for the production of crepe soles. A small amount of raw rubber is being used in erasers, and it is also the chief ingredient of watertight rubber plaster for surgical use. The manufacture of chewing gum represents another use. Raw rubber is employed in the form of adhesive cements for the greatest variety of uses. Solutions of rubber form an indispensable aid for the repair of inner tubes, and also serve as adhesives in the shoe industry, the hat-feather industry and in the fabrication of gummed fabrics (for example, rubber cloaks). Other unvulcanized rubber materials on the market become vulcanized before use, and may therefore be considered intermediate products.

The superiority of the vulcanized product has been the factor which has made rubber especially important in modern manufacture. No other material has been found which is like rubber in its elasticity and other properties. One of the principal applications of rubber today is in the manufacture of shock- and sound-proof articles, such as bumpers, buffers and vehicle tires. Modern fast automobile traffic would not be conceivable without the elastic tire, while the bicycle also owes to the tire its popularity as a means of transportation. All attempts to find a substitute for the tire have been failures. The resistance of rubber to shock and sound is a property which has also been utilized in rubber heels, rubber tips on canes and crutches, rubber flooring and, recently, in various experiments with rubber paving for road surfaces.

The elastic properties of vulcanized rubber are also exploited in rubber bands and stoppers, stamps, elastic thread, belts, and fabric. Rubber sponges and rubber toys are also popular because of these and other properties of rubber.

The relatively high impermeability of vulcanized rubber to gases and liquids makes it suitable for many purposes. Vulcanized rubber is used to a large extent in the fabrication of inner tubes for vehicle tires. Among the many other applications based upon this property should be mentioned (1) gas- and water-tubing; (2) rubber boots; (3) bathing caps; (4) football bladders; (5) hygienic and medical necessities, such as rubber gloves, syringes, air cushions, and ice bags; (6) rubberized fabric which is used for hospital sheeting, for the preparation of rain coats and folding boats, and for airship construction; (7) nipples; (8) rings for sealing bottles and jars; and (9) packing materials for machine construction.

The electrical insulating properties of vulcanized rubber are important for its application in making cables in which copper wire (especially that of large current capacity) is coated with a layer of rubber.

The utility of hard rubber depends especially upon the combination of a horn-like hardness with a certain degree of elasticity. Since hard rubber may

be easily worked and polished, it is a suitable material for combs, tubing, and fountain pens. Hard rubber is not only capable of meeting mechanical requirements, but is also markedly resistant to chemical attack. It is therefore useful for the manufacture of durable articles for medicine, electrotechnology, and photography, and for the lining of iron vats, kettles, pipes, and centrifuges for the chemical industries. It is a necessity for the manufacture of dental goods. Its acoustic properties make it useful for the manufacture of ear-trumpets and wind-instruments, while its electrical insulating properties make it an indispensable material for use in electrotechnology.

These examples give only a hint of the numerous uses for soft and hard rubber; and the possibilities are not nearly exhausted. These materials are employed in the construction of machines and apparatus in so many different ways that it will be sufficient to mention here their use in driving belts, conveyor belts, covers for rolls and shafts, grips (handles), connecting tubes, and blankets for printing. The development of further possible uses in this field is unlimited. The control and stabilization of the price of crude rubber would assist in developing many uses in which the unique properties of the finished products would be of considerable service.

This abundance of technical uses shows clearly that a very extensive specialization has taken place in the modern production of rubber goods. There are few rubber factories in Germany in which all kinds of technical rubber goods are produced; each establishment has to a certain extent its own specialties. For example, some of the largest firms are engaged only in hard rubber manufacture. Others make only hot-vulcanized soft rubber goods, such as tires, or rubber shoes, or toys. Some factories specialize in cold-vulcanized articles, such as cut sheets or dipped goods for surgical articles, etc. Each of these branches of the industry makes use of a manufacturing technique, complete to the smallest detail, which is continually being improved technically as well as economically. In this way, there has gradually been developed a special technology of rubber goods production, which cannot be mastered by any one rubber technician, since the most important advances are often not made public, but are strictly guarded as factory secrets. For this reason, as mentioned in the preface, the description of these specialized techniques must be omitted from this book.

There are, of course, in all factories some well-known fundamental methods of preparation for crude rubber and other raw materials, which are to some degree conducted alike in various plants. A common technology of rubber goods manufacture can therefore be conceived as the foundation of the special technologies just mentioned. Among such primary processing methods, the following deserve consideration:

1. *Washing and drying.* The washing of raw rubber in wash-kettles or on washing mills, and the drying of the washed rubber in ordinary drying-chambers or in vacuum apparatus.

2. *Mastication by mixing-rolls or kneaders.* In this process the dry rubber sheet, fairly tough and having a rough, uneven surface, is converted into a plastic state so that it may be shaped into any form desired. It also becomes tacky and capable of taking up organic and inorganic pigments, especially the sulfur so important in subsequent treatment.

3. *Sheeting or calendering by 2-, 3-, or 4-roll calenders.* The mixed, plasticized material is transformed into a smooth sheet of as nearly uniform thickness as possible, in which form it can be processed into a variety of shapes.

4. *The technique of hot vulcanization.* Comprises heating processes which utilize all of the many types of heating equipment (autoclaves, tube-heaters, platen-presses, etc.), according to the type of process.

5. *The operation of machines and equipment for the preparation of viscous rubber solutions.*

6. *The operation of the "spreading-machine" for the application of rubber solutions to fabric.* The gummed fabric is then used in various branches of manufacture (automobile tires, rubber garments, belts, etc.).

In addition to these common technological processes there are many special manufacturing operations which require unique types of machines and equipment. Finally, technical innovations in processes may become standard practice, or entirely new types of equipment may be introduced. For these reasons it is hardly possible in a scientific treatise to give a thorough and up-to-date description of even the common processes of rubber goods production. Just what changes may be brought about in the near future by the modern direct use of latex, cannot be predicted.

PRODUCTION AND CONSUMPTION—PLANTATIONS

The tremendous increase in the use of rubber may best be estimated by means of statistics of world production and world consumption. These figures, through 1913, are given in Table 3.[30]

TABLE 3.—*World Production and World Consumption.*

Year	World production in tons	World consumption in tons
1890	28,867	26,975
1895	34,277	33,952
1900	53,931	49,181
1905	69,507	65,727
1906	67,918	71,671
1907	68,646	64,528
1908	67,031	67,081
1909	69,372	70,075
1910	70,500	66,000
1911	75,149	73,000
1912	98,929	98,000
1913	108,440	110,000

Of course, these are not absolute values, since they are based upon estimates. The values show that world consumption was only slightly behind production; in some years, for example 1909, consumption even materially exceeded production. This relation was influenced by the enormous development of the automobile industry. These conditions naturally resulted in unusually large price fluctuations, which were intensified by capitalistic speculation. Thus the price of 1 kg. of the best Para rubber was in 1908 about 6.5 M. and advanced in 1910 to 28 M. only to fall soon thereafter to 12 M. The slow decline of prices in the ensuing years will be understood from the explanation which follows.

It is evident that a demand for the opening of new rubber-producing districts would arise from an uncertain market condition caused by lack of raw material. This shortage was relieved to some extent by the long-known proc-

[30] *Gummi-Ztg.*, **24**, 744 (1910); **28**, 160 (1913); **29**, 722, 1013 (1915). For the years since 1913, Table 6 shows that the course of world consumption kept an almost even pace with the growth of world production; that is, world production was artificially adjusted to the consumption.

ess of "reclaiming," in which rubber which had already been made into manufactured products and used as such, was transformed by chemical and mechanical means into a state in which it was suitable for use, either alone or mixed with new rubber, in the fabrication of new goods.

Of more importance were the efforts of all countries having colonies to establish rubber plantations in those of their colonial regions which were suitable for the purpose.[30a] The Marquis of Salisbury (later Secretary of State for India) is credited with having been the first to suggest the planting of rubber in the English colonies. This idea was eagerly accepted by J. Hooker, Director of the Botanical Gardens at Kew. In 1873, James Collins (later Government Botanist in Singapore) was sent by the English government on an investigational tour to the Amazon district, where he was able to collect several hundred *Hevea* seeds. About a dozen of these seeds germinated at Kew and six of the young plants were transplanted in the botanical garden at Calcutta. These plants did not develop and soon died. Undaunted by this failure, Hooker in 1876 communicated with H. A. Wickham, a planter then living in Brazil, and commissioned him to collect a larger quantity of *Hevea* seeds and to transport them to England. Wickham carried out the plan without hesitation, and, with the aid of a number of Tapuyo Indians, he succeeded in collecting the desired material from the best stands of Para rubber trees on the plateaus between the Tapajos and Madeira Rivers. Of especial importance for the transportation of the seeds to England was the fact that at this very time the first steamer to reach the upper Amazon (the S. S. "Amazonas") was lying at anchor there, with no return cargo. By this means, the valuable shipment was taken to Europe by the shortest route and under the most favorable conditions. The "Amazonas" arrived in Liverpool June 14, 1876, and its cargo was rushed to Kew at once. Only about four per cent of the 70,000 seeds gathered by Wickham could be brought to germination in the botanical gardens. About 2,000 of these seedlings were later sent to Ceylon, where they were planted principally in the botanical garden of Paradeniya. From here they were later distributed over the English possessions in eastern Asia.

From these trees and their seeds grew the plantation industry of the Middle East, which today is not confined to the British possessions, but is also well developed in the Dutch possessions. The first four tons of plantation rubber appeared on the world market in 1910. Since that time the cultivation of *Hevea brasiliensis* in the Middle East has increased so greatly and such excellent results have been obtained in regard to the quality of the raw rubber produced, that wild rubber, as a competitor of plantation rubber for the supply of the world market, has become of almost no importance at all. The increasing supply of plantation rubber acted as a price-regulator. When the many new plantings reached a producing age and brought to the market increasing quantities of crude rubber of steadily better quality, the price of plantation rubber, which was at first higher than the price of the Para quality, declined rapidly. This caused a downward movement in the price of wild rubber. The progress of plantation operation and the destructive competition thus presented to wild rubber, are shown by Table 4, in which are tabulated separately the amounts of plantation rubber and of wild rubber marketed in each year since 1910.*

[30a] *Gummi-Ztg.*, **38**, 989 (1924). E. A. Hauser, "Latex," p. 13, Verlag von Theodor Steinkopff, Dresden and Leipzig, **1927**; English translation by W. J. Kelly, p. 11, Chemical Catalog Co., New York, **1930**.

* Translator's Note. Table 5 has been added to show the corresponding statistics for world imports of crude rubber from 1910 to 1932.

TABLE 4.—*Net World Exports of Crude Rubber, 1910-1932.*†

Year.	Plantation									Wild			
	British Malaya. (1)	Netherlands East Indies. (2)	Ceylon. (3)	India. (4)	British North Borneo. (5)	Sarawak. (6)	French Indo-China. (7)	Siam, etc. (8)	Total. (9)	South America. (10)	Other Wild. (11)	Total. (12)	Grand Total. (13)
	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons
1910	6,500	2,400	1,600	200	100	10	180	10	11,000	44,000	39,000	83,000	**94,000**
1911	10,800	2,300	3,200	400	100	30	200	70	17,100	43,000	33,000	76,000	**93,100**
1912	20,300	3,700	6,700	700	200	100	250	150	32,100	49,000	31,000	80,000	**112,100**
1913	33,600	6,400	11,400	1,000	500	150	200	150	53,400	43,000	22,000	65,000	**118,400**
1914	47,000	10,400	15,800	1,300	600	300	200	100	75,700	38,000	8,000	46,000	**121,700**
1915	70,200	20,000	20,800	2,200	1,200	600	400	200	115,600	40,000	11,000	51,000	**166,600**
1916	96,000	33,100	24,400	2,800	1,900	1,000	600	300	160,100	38,000	12,000	50,000	**210,100**
1917	129,000	44,000	31,900	4,000	2,400	1,700	900	400	214,300	41,000	12,000	53,000	**267,300**
1918	112,000	42,000	21,100	4,400	2,600	1,500	500	300	184,400	27,000	10,000	37,000	**221,400**
1919	204,000	85,000	44,800	6,600	3,900	2,200	2,900	600	350,000	39,000	9,000	48,000	**398,000**
1920	181,000	80,000	39,000	6,400	4,100	2,200	3,100	800	316,600	30,000	7,000	37,000	**353,600**
1921	151,000	71,000	40,200	5,300	3,200	2,100	3,600	800	277,200	19,000	4,000	23,000	**300,200**
1922	214,000	94,000	47,400	4,900	3,800	3,800	4,500	1,300	373,700	23,000	3,000	26,000	**399,700**
1923	201,000	117,000	37,100	6,400	4,200	5,700	5,100	2,400	378,900	22,000	6,000	28,000	**406,900**
1924	183,000	149,000	37,400	7,700	4,600	6,700	6,500	2,800	397,700	24,000	7,000	31,000	**428,700**
1925	210,000	189,000	45,700	10,100	5,400	9,000	6,300	4,000	479,500	28,000	11,000	39,000	**518,500**
1926	286,000	204,000	58,800	9,900	5,800	10,000	7,400	4,000	585,900	25,000	11,000	36,000	**621,900**
1927	242,000	229,000	55,400	11,300	6,600	11,000	8,000	4,000	567,300	29,000	11,000	40,000	**607,300**
1928	299,000	229,000	58,000	10,800	7,000	11,000	9,000	5,000	628,800	21,000	7,000	28,000	**656,800**
1929	455,500	255,500	80,300	11,700	7,400	11,300	10,100	5,100	835,500	21,100	4,900	26,000	**862,900**
1930	442,700	240,900	75,600	10,800	7,100	10,300	10,300	4,300	801,700	14,300	4,500	18,800	**820,800**
1931	422,000	257,200	62,300	8,500	6,200	10,500	11,700	4,500	782,900	12,100	2,100	14,200	**797,100**
1932	405,700	211,100	49,300	3,900	5,400	7,000	14,400	3,500	700,300	6,400	1,300	7,700	**708,000**

Note.—Most of the figures in this table have been obtained from official sources. The exports of Plantation Rubber have been adjusted to allow for moisture, etc., in native rubber and for rubber smuggled out of Malaya during the period of regulation of exports.

† *Bull. Rubber Growers' Assoc.*, **15**, 577 (1933).

TABLE 5.—*Net World Imports of Crude Rubber, 1910-1932.*†

Year.	United Kingdom. (1)	* France. (2)	Italy. (3)	Austria and Germany. (4)	Hungary. (5)	Russia. (6)	Holland. (7)	Belgium. (8)	* Scandinavia. (9)	Spain. (10)	United States. (11)	* Canada. (12)	* Japan. (13)	Australia. (14)	Other Countries. (15)	Total. (16)
	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons
1910	20,500	3,800	1,800	13,700	2,000	6,000	1,800	2,200	1,100	400	42,200	1,500	700	400	300	**98,400**
1911	16,700	5,400	2,400	15,100	2,300	6,000	1,400	2,000	1,300	500	41,900	1,700	900	500	400	**98,500**
1912	18,700	4,600	3,300	15,400	2,600	7,000	1,400	2,500	1,400	400	56,000	2,500	900	600	400	**117,700**
1913	25,300	6,500	2,500	16,300	2,800	12,000	2,400	3,600	1,200	600	52,200	2,200	1,200	800	400	**130,000**
1914	18,500	5,000	2,700	11,000	1,900	11,000	1,800	1,500	1,300	600	62,300	2,500	1,000	1,000	300	**122,400**
1915	15,100	10,800	5,000	4,000	500	13,000	2,900	.....	2,000	1,000	99,000	4,400	1,700	1,500	400	**161,300**
1916	26,700	14,700	4,800	2,000	500	9,000	200	.....	1,800	1,700	117,600	4,500	3,000	1,500	500	**188,500**
1917	26,000	17,000	5,600	1,000	100	5,000	.....	.....	800	1,300	179,300	6,200	3,700	2,000	400	**248,400**
1918	30,100	18,000	7,100	.....	.....	.....	.....	.....	700	800	143,400	8,300	7,300	3,000	1,100	**219,800**
1919	42,700	20,100	9,900	4,500	300	100	3,800	4,000	3,200	3,700	238,400	8,800	10,000	3,500	1,800	**353,800**
1920	56,800	16,300	6,100	12,600	1,300	100	5,500	3,400	2,300	2,000	249,500	11,900	6,000	3,500	1,300	**378,600**
1921	42,100	14,800	3,900	21,600	2,400	200	1,000	1,700	1,300	2,200	179,700	8,200	21,000	3,000	1,300	**304,400**
1922	11,700	27,700	6,400	27,600	2,600	3,100	−3,800	200	1,700	600	296,400	9,400	15,000	2,500	1,800	**402,900**
1923	12,700	28,600	8,500	18,500	2,600	4,500	800	2,200	2,200	600	301,500	13,200	16,000	2,000	2,900	**416,800**
1924	−11,600	31,700	8,800	22,700	2,600	1,500	−800	2,700	2,900	900	319,300	14,400	19,700	2,600	3,800	**421,200**
1925	4,100	34,300	11,400	33,900	2,500	7,500	900	2,900	2,800	1,200	385,600	19,800	12,900	4,500	4,300	**528,600**
1926	84,900	35,700	9,800	22,800	2,800	7,000	2,700	2,500	3,300	1,100	400,000	20,200	18,300	9,000	4,400	**624,500**
1927	60,200	35,700	11,300	38,900	3,900	14,000	600	6,500	3,400	1,300	403,500	26,400	20,500	9,500	6,900	**642,600**
1928	4,800	38,000	12,400	37,900	4,400	8,000	2,200	7,900	3,700	2,100	407,300	30,900	25,800	8,400	9,700	**603,500**
1929	122,700	61,800	16,400	49,100	4,700	12,700	3,200	9,400	5,500	2,100	528,600	35,500	34,300	15,900	14,700	**916,600**
1930	120,100	71,400	18,600	45,500	3,800	16,700	2,900	10,700	6,700	3,300	458,500	28,800	32,700	5,400	14,300	**839,400**
1931	85,200	47,700	10,100	39,200	4,500	30,700	2,200	11,000	5,600	2,600	477,100	25,300	43,500	7,600	21,000	**813,300**
1932	44,100	41,700	15,300	45,000	2,400	30,000	2,800	9,500	6,600	4,300	393,800	20,900	56,000	12,400	21,800	**706,600**

* Including Gutta Percha.

Note.—Most of the figures in this Table have been obtained from official sources. Several of the countries prior to 1914 included Reclaimed and Scrap Rubber amongst their imports of Crude, and a few countries may do so still.

† *Bull. Rubber Growers' Assoc.*, **15**, 586 (1933).

It seems fitting to discuss briefly here the question as to whether there was a demand during the post-war period corresponding to this rapidly mounting increase in production of raw material. This question is answered to some degree by Table 6.[31]

TABLE 6.—*World Production and World Consumption Since 1920.*

Year	World production in tons	World consumption in tons
1920	370,000	310,000
1921	282,000	265,000
1922	400,000	386,000
1923	382,000	434,000
1924	420,000	475,000
1925	500,000	552,000
1926†	614,778*	533,915**
1927†	605,196*	589,128**
1928†	649,674*	667,027**
1929†	863,410*	785,475**
1930†	821,815*	684,993**
1931†	797,441*	668,660**

* Net Exports. ** Estimated.

†Translator's Note. Figures for 1926-1931 inclusive are added by the translator from *India Rubber World*, **86**, No. 1, 90 (1932), credited to W. H. Rickinson & Son.

The values given for world production vary considerably from those in Table 4, which are taken from a different source. The discrepancy demonstrates the well-known fact that all statistics of world production and total consumption are subject to various errors and thus differ from each other. These differences may be neglected in Table 6 for the present purpose, since the amounts here given for production and consumption originate from the same source.

THE PRICE TREND OF THE WORLD RUBBER MARKET

As may be seen from the above tables, the plantation industry faced a crisis in 1920-22. The planters had built up exaggerated hopes which were based upon the growing needs of a Europe hungry for merchandise and upon the enormous demand caused by the frenzied development of the automobile in the United States. However, because of the widespread industrial crisis of the post-war years, these expectations were not realized. The price of crude rubber declined and reached a level that seemed to endanger the profitableness of plantation operation. Instead of a decrease in the production of raw material, over-production occurred, and an increasing amount of storage resulted. Confronted with this situation, the British Colonial Commission attempted to relieve the condition. The Stevenson Restriction Scheme* of November 1, 1922 proposed to regulate the export of the English rubber-producing districts, to harmonize supply and demand, and to stabilize the price of rubber upon the basis of 21 pence per pound. According to this restriction plan, each plantation was allowed to export only a certain percentage of its normal production, under penalty of a great increase in export duty. This percentage, the so-called "production quota," was fixed for each quarter according to the level of the price of rubber and the extent of world reserves.

[31] *Gummi-Ztg.*, **41**, 809 (1926).

* Translator's Note: A more complete account of the historical background and effects of the restriction scheme is found in J. C. Lawrence's book, "The World's Struggle with Rubber, 1905-1931," Harper & Brothers, New York, **1931.**

The results of this scheme may be seen in Table 7, which shows the price movement of the ensuing years.[32]

TABLE 7.—*Price Movement Since the Restriction.*

Year	Approximate price per kg. raw rubber in RM
1920	6.50
Beginning 1921	2.80
Middle 1922	1.30
Beginning 1923	3.50
Middle 1924	1.80
Beginning 1925	3.50
End 1925	10.50
End 1926	3.50
Beginning 1927	3.50

TABLE 8.*—*Average Spot Closing Prices for Ribbed Smoked Sheets (New York Market) 1910-1932.*

Year	Cents per lb.	Year	Cents per lb.
1910	206.60	1921	16.36
1911	141.30	1922	17.50
1912	121.60	1923	29.45
1913	82.04	1924	26.20
1914	65.33	1925	72.46
1915	65.85	1926	48.50
1916	72.50	1927	37.72
1917	72.23	1928	22.48
1918	60.15	1929	20.55
1919	48.70	1930	11.98
1920	36.30	1931	6.17
		1932	3.49

* This table has been added by the translator [*Rubber Age (N. Y.)*, **34**, 137 (1933)].

A slight increase in price was the immediate consequence of the restriction. During 1925 there occurred a sudden, rapidly increasing demand for rubber because of the development of the automobile industry. The restriction, now in force for two years, was also having its effect. The price quickly rose, and the emergency seemed to have been surmounted. However, this condition was not maintained, for the price advance brought about a considerable increase in production in all districts not under English control, and particularly in the Netherlands East Indies. Besides, the restriction plan seemed to have accomplished its purpose, and the British Colonial Commission, believing that the Stevenson Scheme could be modified, greatly increased the export quota. Table 9 shows the distribution of world production over the different colonial districts in 1922 and 1923.[33]

The situation today is distinctly more unfavorable to England, since not more than 55 to 60 per cent of the total world production is under British control.

The growth of competition from non-British producers in the world market was the one factor which led to the failure of the Stevenson Scheme. The greatly increased production thus brought about was not followed by any equally great consumption. Because of the high prices of 1925, the coun-

[32] *Gummi-Ztg.*, **42**, 358 (1927).

[33] *Gummi-Ztg.*, **38**, 983 (1924). See also Table 4.

TABLE 9.—*World Production by Colonial Districts.*

District	1922 Production, tons	1923 Production, tons
Malacca	212,694	175,000
Ceylon	47,637	35,000
Netherlands East Indies	99,856	133,000
Indo-China	4,104	5,000
British East Indies	4,854	6,500
Borneo	3,750	13,500
British Borneo, Congo, and other districts	6,634	

tries which were the most important consumers had fallen back upon the well-known substitutes for rubber. The reclaiming of old rubber flourished again, and in the United States the consumption of reclaimed rubber increased from 73,000 tons in 1924 to 114,000 tons in 1925, and 150,000 tons may not be too high an estimate for 1926. Some of the plantation companies profited considerably from the restriction, but the real objective of the scheme —price stabilization—was never realized. Even if new expedients had been planned by the English, they could have been only partially successful as long as the planters in the Dutch Indies remained outside the restriction scheme. It appeared doubtful that the price stabilization sought by England could be reached under the circumstances, because of the favorable position of the producers in the Dutch Indies.

Therefore, the Stevenson plan was abandoned by decree of the English government November 1, 1928. In any case, the greatest benefits of this plan had not fallen to the British plantation owners, but to those who had not allied themselves with the restriction—the Dutch planters. The high prices caused by the restriction had also resulted in the rapid development of the cultivation of *Hevea* trees in other countries. It became evident that the Americans were trying to free themselves more and more from British domination by buying plantations and setting out new plantings on a gigantic scale. Thus the Goodyear Tire and Rubber Company now has at its disposal a plantation area of 71,659 acres in Sumatra, while great rubber plantations have been laid out by Firestone in Liberia and by Ford in Brazil.*

THE PREPARATION OF SYNTHETIC RUBBER AND ITS APPLICATION IN THE WORLD WAR

Because of the growing consumption of rubber since 1890, the interest of science has been drawn to the problem of increasing the amount of this raw material by its preparation through synthesis.

The historical development of the synthesis of rubber and the chemistry of the various kinds of artificial rubber are thoroughly treated on p. 240 of the section on "The Chemistry of Rubber." It may be mentioned here that one of these artificial products, called dimethylbutadiene rubber, or "methyl-rubber" (cf. p. 243) has rendered especially important service to the German people. When Germany was cut off from the supply of urgently needed natural rubber soon after the World War began, the manufacture of the comparatively expensive artificial product was begun on a factory scale. It was used alone or in mixtures with reclaimed rubber to be made into rubber.

* Translator's Note. The following plantation areas were controlled by American firms at the end of 192[illegible] [illegible]: *India Rubber Age (N. Y.)*, **27**, 416 (1930)]:

Ford Industrial Co. of Brazil—3,700,000 acres in Para.

Firestone Plantations Co.—1,002,000 acres in Liberia.

U. S. Rubber Plantations, Inc.—135,160 acres in Sumatra and British Malaya.

Goodyear Rubber Plantations Co.—82,500 acres in Sumatra and the Philippine Islands.

goods necessary for military purposes. One of the most interesting practical applications of these synthetic products was in the manufacture of tires for automotive vehicles. The accomplishments of German science and rubber technology, in characteristic cooperation under the inexorable pressure of military necessity during the last two years of the war, deserve full exposition in a treatise on the science of rubber. However, lack of space and other reasons have required that it be omitted here. Only a few of the characteristic phases of this development, which have been mentioned in the preface, and in which the editor has been especially interested, will be described at this time.

During the last year of the war, methyl-rubber was manufactured in large quantities in two modifications: the so-called "H-rubber" and the "W-rubber" (*see* p. 245). These modifications exhibited quite different physical properties and required different technical manipulation in factory processing. The vulcanizates from both kinds of artificial rubber were always leather-like in quality and were less elastic than natural rubber vulcanizates. This lack of elasticity persisted in spite of all precautions and constituted a great disadvantage of methyl-rubber vulcanizates as compared with natural rubber vulcanizates. The contrast was particularly noticeable in cold weather. The elasticity (especially of the H-rubber vulcanizates) could be improved to some extent by the addition of certain organic materials. This knowledge made possible the first approach to the application of methyl-rubber for the manufacture of automotive tires. The technical foundation for the use of methyl-rubber on a laboratory scale was thoroughly developed at the Materialprüfungsamt with the cooperation of Dr. Gottlob, then a chemist at the Elberfelder Farbenfabriken. By means of comprehensive technological experiments in many rubber factories, this knowledge was later put into practice for the manufacture of tires.

No great difficulty was experienced in applying H-rubber to the manufacture of hard rubber. The vulcanizates could be readily worked and polished, they were sufficiently strong, and were even superior to the natural rubber product in their resistance to electrical breakdown. H-rubber became a very useful substitute for hard rubber during the war, and was used in large quantities for the preparation of storage battery boxes and other articles.

Considerably greater difficulty was experienced in the application of methyl-rubber to the manufacture of tires and soft rubber goods in general. The solubility in benzene or gasoline necessary for the fabrication of tires was possessed only by W-rubber, and even this rubber gave only fairly homogeneous, clear solutions. Its cements were also much less tacky and adherent than those of natural rubber. Dried coats retained their tackiness only a short time, and the immediate processing of coated fabric was therefore necessary. Although a host of difficulties was encountered in the attempt to master in some degree the problem of applying methyl-rubber to the manufacture of articles necessary for war, this strenuous and laborious cooperation was not entirely fruitless from the standpoint of science and technology. It is no longer a secret that shortly before the end of the war it was firmly believed that the emergency of tire requirements for German military vehicles had been mastered. Further development went forward with less trouble than was expected. If, at a later date, it had become possible to maintain the efficiency of the factories and equipment for the manufacture of synthetic rubber, the demand could have been met for truck and passenger tires which would have been, under the circumstances, fairly serviceable as "replacement"

tires. In view of the possible future development of the production and application of synthetic rubber, these facts deserve to be permanently recorded because they indicate the progress which can be made in the future in the production and technical application of synthetic rubber by the unceasing advance of our chemical science.

After the war, the industrial preparation of synthetic rubber was abandoned for the time being. Its manufacture in competition with natural rubber promised little success because of the manufacturing cost, the severe decline in price of natural rubber following the vigorous development of plantation culture, and the serious defects inherent in the artificial product. However, the interest in the synthesis of rubber did not subside, and the work is still advancing in scientific laboratories, as is shown on pages 240 to 269 of the section on "The Chemistry of Rubber."

Progress seems to have been made in this field especially with respect to the production of raw materials for the manufacture of the synthetic product. A. von Weinberg,[34] in an address on the occasion of the fiftieth anniversary of the Verein zur Wahrung der Interessen der chemischen Industrie Deutschlands in November, 1927, made the following statement: "Contact synthesis enables us to obtain the starting materials for the synthesis of rubber and gutta-percha in more convenient fashion. We can begin at once with a rational production." It is also evident that clear-sighted effort is continuing, and it is hoped that this difficult problem will also be mastered by the large-scale chemical manufacturing processes already successful in so many fields.

Newer Methods in Vulcanization Technique—Outlook

The difficulty of improving the quality of synthetic rubber was to become of the greatest importance for the processing of natural rubber. Some of the rubbers obtained by synthetic methods exhibited one of the undesirable properties of natural rubber, in that they absorbed oxygen and decomposed rather quickly in air. It was found in the Farbenfabriken vorm. Bayer and Company that this objection could be overcome by the addition of small amounts of organic bases to the artificial products. Piperidine and other compounds were used as protecting bases ("antioxidants"). It was noticed in these experiments that not only was oxidation inhibited by such substances, but also that rubber-sulfur mixtures containing piperidine showed, after heating, a much higher combined sulfur content than was ordinarily to be expected. Similar experiments with natural rubber led to the same result. Thus the first organic accelerator was found.* This was followed by the discovery of many others in later years, but only a comparatively small percentage of these attained practical utility. It had long been known that certain inorganic materials such as litharge accelerated the vulcanization process, but the new organic accelerators proved to be even more effective. When added in the small amounts of 1 to 2 per cent of the rubber-sulfur mixture, they very appreciably decreased the time necessary for vulcanization. This result brought about an important saving of fuel and mold materials and had other practical advantages. Other compounds were later found which not only made possible a shorter heat treatment but also a lowering of the temperature

[34] *Chem.-Ztg.*, **51**, 894 (1927).

* Translator's Note. Cf. W. C. Geer and C. W. Bedford, *Ind. Eng. Chem.*, **17**, 393 (1925), who credit the discovery of organic accelerators to George Oenslager in 1906. See also George Oenslager, Perkin Medal address, *Ind. Eng. Chem.*, **25**, 232 (1933). D. Spence, *J. Soc. Chem. Ind.*, **36**, 118 (1917) and *J. Ind. Eng. Chem.*, **10**, 115 (1918), claims priority for the use of piperidine as an accelerator.

of vulcanization to a point as low as room temperature. Therefore, it seemed that such substances acted not only as vulcanization accelerators, but especially as agents for improving the quality of the vulcanizate, since through their use the rubber was subjected to less severe treatment in vulcanization, and the vulcanizates possessed mechanical properties which had never before been attained. To the war-time task of improving the properties of synthetic rubber we owe the discovery which has become of the utmost importance to the rubber industry in every respect, and which has directly revolutionized manufacturing procedure. As can be seen from the ever-increasing patent literature on this subject, its development is not at an end, and what the future will bring cannot be foretold.

It is now easily realized that this new knowledge attracted attention in the widest circles of scientific work to the problem of vulcanization and to the explanation of many other phenomena which were long known but not well understood. After the discovery of accelerators, the literature of rubber, which up to that time was comparatively narrow in range, expanded rapidly. Within the last decade, numerous researches in chemical and physical fields have been conducted with the object of reaching a better understanding of the many problems which are scattered over the whole realm of rubber. The sections to follow clearly show that these investigations have indeed increased our knowledge essentially, but we still seem far from a solution of the remaining problems. Further serious and laborious scientific effort will be required before the riddle of rubber will have been solved completely.

Botany, Cultivation, Collection and Preparation of Rubber

By A. Zimmermann*

The Rubber-producing Plants; their Distribution and their Cultivation

Introduction

Natural rubber is obtained exclusively from the milky juice, or so-called latex, of plants. The plants which yield latex can be easily recognized since they exude a turbid juice when wounded. The wolfsmilk (spurge) is an example of such a plant. Although the milk-like juice is usually white, it may be intensely colored. In the case of *Chelidonium majus*, for example, the latex possesses a golden-yellow color.

Relatively few of the numerous latex-yielding plants are suitable sources of rubber. In most of them, the rubber hydrocarbon is either missing or else present in such a small proportion that the production of rubber is not feasible. A. J. Ultee[1] has recently proved that substances of the nature of rubber or gutta-percha may be entirely missing, even in the very turbid latices of many species, such as *Artocarpus clastica* and *Broussonetia papyrifera*. All latex-producing plants of the cold and temperate zones are characterized by their small rubber content. Even in the tropics and subtropics, only a few of the numerous plants producing latex contain appreciable quantities of rubber, and among these moreover only a portion are capable of yielding rubber which will meet the high requirements of a good commercial product. In the cases of many of these plants, furthermore, the rubber hydrocarbon of the latex is mixed with so much foreign matter, especially resinous compounds, that the rubber obtained can only be used commercially for the lower grades of products. Such rubber is used extensively in manufacturing only when it is supplied at a very low price and when a shortage of first class rubber prevails in the market.

Up to the end of the Nineteenth Century, the rubber appearing on the world market originated almost exclusively from wild stock, which is widely distributed throughout many tropical regions. In the present century, however, the plantation-grown rubber trees have played a role of ever-increasing importance. It was predicted in the early days that over a long period of time plantation rubber would never be able to compete with wild rubber, since

* Translated by V. N. Morris and H. W. Greenup.

[1] *Bull. jard. bot. Buitenzorg*, [3], **6**, 264 (1924).

the cost of establishing and maintaining a plantation would have too adverse an effect on the profits to be derived from the enterprise. As a consequence of the use of the methods of cultivation and tapping developed in the Middle East, however, the cost of converting latex into crude rubber is considerably smaller than is the case with most kinds of wild rubber. With the latter, the cost of obtaining the rubber is greatly increased by the fact that the rubber trees are seldom found growing in dense groves and are generally located in regions so difficultly penetrable that transportation costs are high. The existing trees have often been tapped by the natives in such an irrational manner that their capacity for yielding rubber has been either greatly impaired or entirely lost. In this connection, an exception must be made in the case of the large stands of *Hevea* trees (the most important rubber-yielding plant of the Amazon region), the yield capacity of which has remained unchanged for a long time, despite the poor methods of tapping used. Further factors contributing to the high cost of wild rubber include the difficulty of transportation to the shipping points on the coast, and the unsatisfactory situation of the trees, which are under water at times and are thus cut off from all traffic with the outside world. Experience has actually proven that, under favorable conditions, plantation Hevea rubber can be brought on the market at much less expense than wild rubber. The difference in price between the wild and plantation grades of Hevea rubber has been decreased more and more in recent years.

The enormous expansion in the number of *Hevea* trees since the beginning of the present century has resulted in the world market being ruled by this species. In fact, the growth of other kinds of rubber-producing trees has been repressed. Whether Hevea plantation rubber will be able to maintain its dominating position in the future cannot be predicted with certainty, however. It is conceivable, for instance, that the cost of labor might some time be increased in certain districts (as a consequence of economic or political revolution) to such an extent as to influence profits very unfavorably. Furthermore, there is no assurance that a devastating disease may not some time attack the *Hevea* trees (as was the case in Dutch Guiana several years ago) and thus reduce or eliminate all profits from the operation of the plantations.

To become familiar with rubber plants other than *Hevea* would seem to be a matter of historical interest only, were it not for the fact that in case of such a rise in the price of rubber as took place in 1925, for instance, wild rubber, including rubber from other species (*Manihot,* for instance) will be brought regularly into the market. In that which follows, therefore, a review is given of the species producing wild rubber and also of the species other than *Hevea* cultivated on plantations, the discussion being limited to the most important rubber-bearing plants. Too much space would be required to cover all the plants from which rubber has been obtained, or in whose latex rubber has been found. In this connection, the reader is referred to the compilation in the fourth edition of J. V. Weisner's "Die Rohstoffe des Pflanzenreichs,"[2] in which literature references to 490 different species are listed.

Wild Rubber

The plants yielding wild rubber are grouped according to their geographical distribution in the discussion which follows, a beginning being made with

[2] Vol. 2, p. 1705, W. Engelmann, Leipzig, 1928.

those of South America, the country which has always produced the greatest amount of wild rubber for the market.

South America

The largest portion of the South American wild rubber originates in the districts drained by the Amazon River and its tributaries. The area of the territory in which rubber trees grow is estimated to be about 2,250,000 square miles, of which 1,486,900 are in Brazil, 200,000 in Bolivia, 225,000 in Peru, 100,000 in Equador, 150,000 in Colombia and 30,000 in Venezuela. The quantity of rubber exported from this field reached a maximum of 45,067 tons in 1912. In succeeding years a more or less steady decrease took place, the tonnage being but 20,159 in 1921.*[3]

Not inconsiderable quantities of rubber have also been produced in Brazil outside the Amazon district, especially when rubber prices were high. This production amounted to about 400 tons in 1912, but decreased to 257 tons in 1921.

By far the major portion of the rubber produced in the Amazon territory is obtained from the different species of *Hevea*. Second in importance among rubber-producing trees is the *Castilloa Ulei*. In the regions outside of the Amazon territory, the rubber produced is largely from the different species of *Manihot* and from the *Hancornia speciosa*. In the year 1901, for instance, there were exported from the Amazon field 14,659 tons of Hevea and 3,732 tons of Castilloa rubber. Further exports from Brazil included 473 tons of Manihot and 394 tons of Hancornia rubber.

Hevea. The genus *Hevea* belongs to the family of Euphorbiacae or wolfsmilk (spurge) plants. This genus embraces numerous species, which are to be distinguished from the native varieties of wolfsmilk, in that they form trees of considerable height. In the case of *Hevea brasiliensis*, the most important plant from the standpoint of rubber production, trees 30 meters high and 2.5 meters in circumference are not uncommon. In fact, individual trees have been known to attain a height of 45 meters and a circumference of 4.8 meters. The dense foliage of these trees (Fig. 1) consists of triple long-stemmed leaves, which are discarded once every year, leaving the trees entirely bare. This so-called "wintering," the occurrence of which is primarily dependent on the rainfall, generally lasts only a short time. Simultaneously with the new foliage appear the rather unattractive flowers, which are united into composite leafless panicles. (Fig. 2.) Male and female flowers are to be distinguished, both being found on the same branch. The number of the male flowers is always much greater (60 times on the average) than that of the female flowers. The perianth of the female is somewhat smaller. In both kinds of flowers the perianth has a more or less intense yellow color, and a bell shape with five lobes. In the center of the male flower is to be found the androecium, with two whorls of five sessile anthers each. (Fig. 2, III). The androecium grows with the rudimentary ovary which rises above it. The female flowers stand at the ends of the axes of the inflorescences. In them is to be found (Fig. 2, IV) at the lower end of the ovary, a small disc with ten small elevations which are apparently rudimentary stamens. The triple ovary carries at the top three stalkless stigmas and contains in every case a seed foundation, from which

* Translator's Note. These exports amounted to 28,768 tons in 1927 and 6,450 tons in 1932, according to the United States Department of Commerce. V.N.M.

[3] See *U. S. Dept. of Commerce, Trade Promotion Series*, 23, 1 (1925). This work also contains considerable statistical material in connection with rubber production in the Amazon territory.

Figure 1—*Hevea brasiliensis* in the experimental gardens at Buitenzorg (Java).

the seeds develop. The walls of the ripe fruit are pulpy on the outside and hard as stone on the inside. When the fruit dries out a hygroscopic tension develops in the hard layer of the fruit wall. This eventually leads to a sudden dehiscence which results in the seed being thrown out for some distance. The ripe seeds are surrounded by a leathery spotted shell and contain in the median plane a large embryo, embedded in an oil-rich nutritive tissue (perisperm). The quantity of oil in these seeds is great enough to justify a demand for them as a raw material in the production of oil.

Hevea brasiliensis is to be found especially in the delta of the Amazon River and in the region of the tributaries emptying into it from the south. Its occurrence here is not limited to the territories flooded by the rivers (despite frequent statements to the contrary). In fact, according to H. A. Wickham,[4] J. Huber,[5] and W. L. Schurz, O. D. Hargis, C. F. Marbut and C. B. Manifold,[6] *Hevea brasiliensis* thrives better in general on the plateaux which are not exposed to annual flooding. It should be emphasized at this point that the seeds, which were collected by H. A. Wickham in 1876, and

[4] Wickham, H. A., "On the Plantation, Cultivation and Curing of Para Indian Rubber," London, **1908**.

[5] Huber, J., "A seringueira (Hevea brasiliensis Müll. Arg.)," p. 10, Instituto Lauro Sodré, Para, **1907**.

[6] *U. S. Dept. Commerce, Trade Promotion Series*, **23** (1925).

from which the plantation industry of the Middle East developed, were obtained on the plateaux situated between the Madeira and Tapajoz Rivers.

To the north of the Amazon River is to be found almost exclusively *Hevea Benthamiana,* which likewise yields a very good rubber. *Hevea guyanensis* is distributed throughout the Amazon region. It yields considerably less rubber than the two previously mentioned species, however, and the rubber is less valuable commercially. This applies also to the other species of *Hevea* not mentioned here.

None of these species is to be encountered in the Amazon region in dense groups. They are rather to be found standing alone in forests made up of many different kinds of trees. More than 8 *Hevea* trees are seldom located in a hectare of virgin forest.

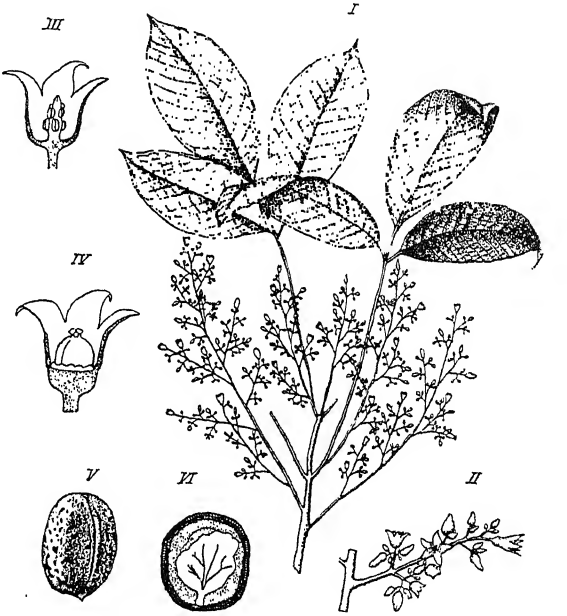


Figure 2—

Hevea brasiliensis.

I. Blooming branch.
II. Panicle (showing flowers).
III. Male flower.
IV. Female flower.
V. Seed.
VI. Cut section of seed.

(According to O. Warburg and N. L. Swart and A. A. L. Rutgers.)

The average yield of one tree is about 20 grams per day and 2 kg. per tapping season, according to E. Ule.[7] Individual trees are said to give up to 200 grams in a day and 12 kg. in a year. The productive life of the tree is said by Ule to be at least 20 years.

The rubber obtained from the different species of *Hevea* is generally designated as Para rubber in the market. This name is derived from the fact that the city of Para (now called Belem), which is located not far from the mouth of the Amazon River, forms the commercial center for this type of rubber. More recently, however, Manaos, which is situated on the Amazon near the mouth of the Negro River, has become more and more of a collection point for rubber. The city of Iquitos, located not far from the Brazilian border, forms a commercial center of increasing importance for the rubber collected in Peru.

Castilloa. Of the genus *Castilloa* (often designated in the recent American literature as *Castilla*), which belongs to the Moraceae family, only one kind,

[7] *Tropenpflanzer Beihefte,* 6, 44 (1905).

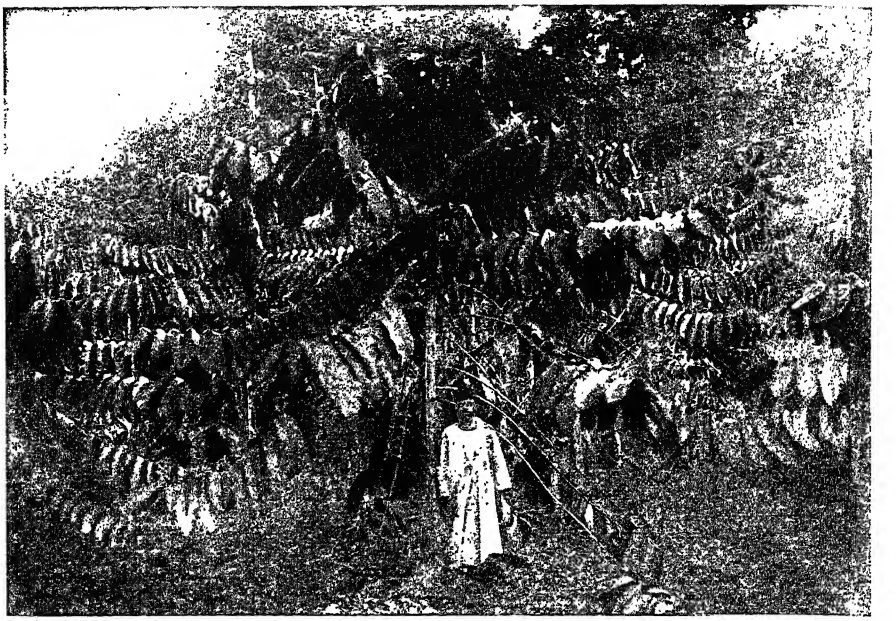


Figure 3—*Castilloa elastica.* Three-year-old tree.

Castilloa Ulei, occurs in the Amazon region and the territory bordering it on the north. *Castilloa Ulei* trees are to be found particularly in the Andes and the higher mountain districts. The trees attain approximately the same dimensions as those of the *Hevea brasiliensis.* The young *Castilloa* trees are characterized, however, by having side branches which stand approximately horizontal, and which are bent downwards somewhat at the ends (Fig. 3). Upon further development these branches are thrown off, beginning with the lowest ones, and branches directed obliquely upwards then develop. These latter lead to the formation of a crown. The leaves, which may be up to 30 cm. in length, are short stemmed.

The flowers (Fig. 4) are, as with the related fig, united into pulpy inflorescences. These latter are not closed in the case of *Castilloa,* although they are more or less arched. Male and female flowers are to be found in separate inflorescences but on the same tree. The fruits are surrounded by pulpy hulls, and have seeds which are about the same size as a pea and which are rich in oil.

Since the trees are generally felled in obtaining the rubber, they have become almost completely exterminated in many districts, where they formerly abounded. That Castilloa rubber has nevertheless not yet disappeared from the world market is due primarily to the fact that new districts containing *Castilloa* trees are continually being exploited.

The rubber derived from the different species of *Castilloa* is usually designated as Caucho and appears on the market in the form of "Balls," "Slabs," or "Strips."

Manihot. Like *Hevea,* the genus *Manihot* belongs to the Euphorbiaceae family. Among the representatives of this genus is the Maniok (*Manihot*

utilissima and other species), which is cultivated extensively in the tropics on account of its starch-rich tubercles. In contrast to these shrub-like plants,

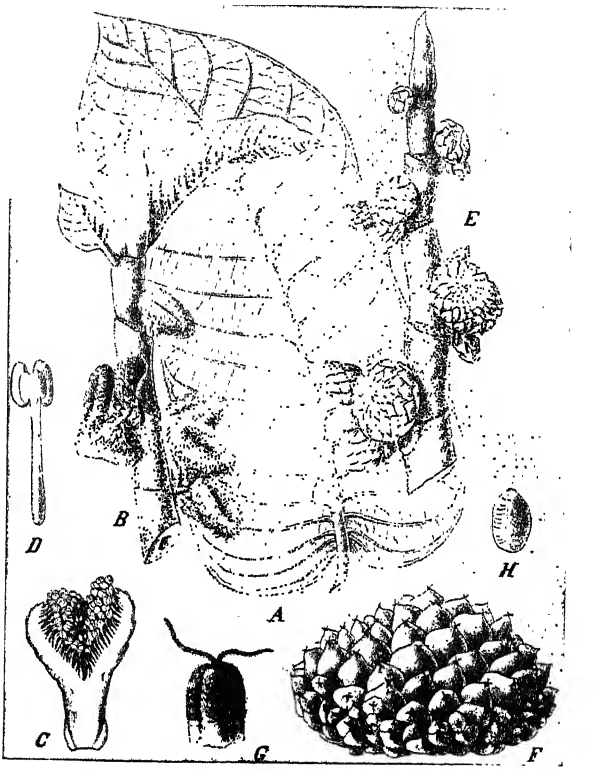


Figure 4—

Castilloa elastica.

A. Leaf.
B. Branch with male flowers.
C. Cut section of male inflorescence.
D. Stamen.
E. Branch with female flowers.
F. Arrangement of fruit on stem.
G. Female blossom.
H. Seed.

(Courtesy of O. Warburg.)

the varieties yielding rubber take the form of tall trees (Figs. 5 and 6). The most important of these is *Manihot Glaziovii,* which is distributed especially throughout the states of Ceará, Rio Grande del Norte and Parahyba. The leaves of this plant are hand-shaped, usually with three to seven "fingers" (*see* Fig. 7), and are spread out in a shield-shaped arrangement over the stem. Male and female flowers are to be found on the same inflorescence. The male flowers are considerably smaller than the female and contain ten stamens and a star-shaped nectary at the base. In the female flower is to be found a triple ovary, which carries three almost hemispherical stigmas, which are fringed around the edges. The fruit is a three-seeded capsule, the walls of which fall to pieces on drying. As with the *Hevea,* the seeds are hurled forth in the process. The somewhat flattened seeds are dark in color and rich in oil. The rubber derived from *Manihot Glaziovii* appears on the market under the name of Ceara or Manicoba rubber.

The less important rubbers include (1) "Jequie Rubber," obtained from the *Manihot dichotoma,* which grows especially in the southeastern part of the state of Bahia in the vicinity of the little city of Jequie; (2) "Manicoba de Sao Francisco," derived from the *Manihot heptaphylla* and encountered in Bahia on the right bank of the Sao Francisco River; and (3) "Manicoba

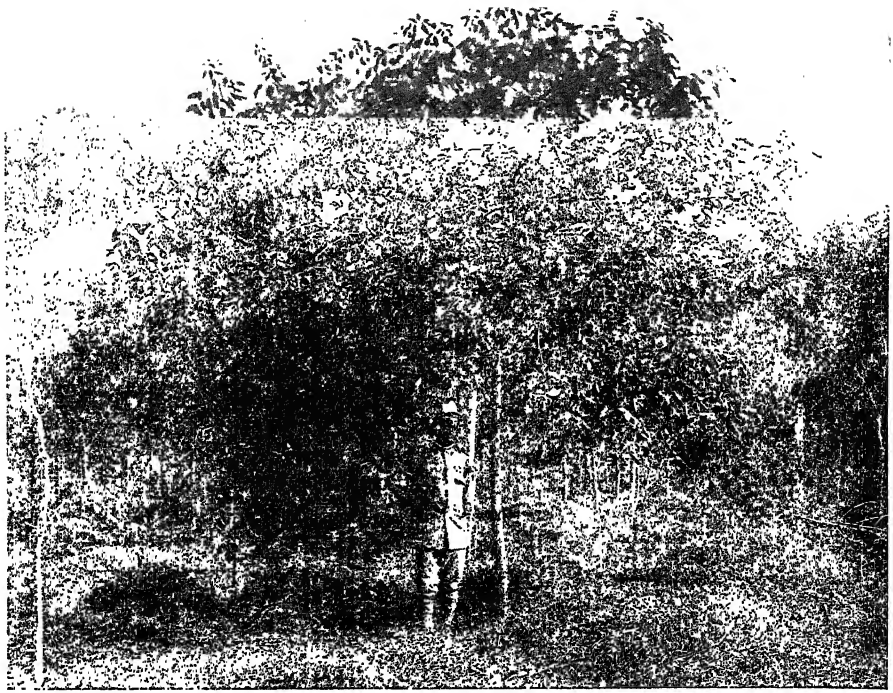


Figure 5—*Manihot glaziovii.* Young trees.

de Piauhy," obtained from the *Manihot piauhyensis,* which is to be found especially in the southeastern part of the state of Piauhy.[7a]

Hancornia. The genus *Hancornia* belongs to the Apocynaceae family, and contains only one species, *Hancornia speciosa,* a small tree with loosely hanging branches. It is cultivated considerably from Paraguay to Venezuela on account of its fruit, which has a pleasant taste. The rubber from this tree is designated as "Mangabeira Rubber." It is obtained particularly from southern Brazil, from which district it also comes on to the market under the name of "Santos Sheets" or "Rio Sheets."

Sapium. The rubber usually designated as "Caucho blanco" is obtained from different species of the genus *Sapium,* which belongs to the Euphorbiaceae family and which is found in the northern part of South America. Thus in the Amazon district are to be found *Sapium verum* and *Sapium tapuru,* and in Colombia, *Sapium biglandulosum* and *Sapium Thompsoni.* The latter, which at the present day seems to be almost exterminated, yields the highly prized "Colombia virgen." The rubber originating in British Guiana is derived principally from the *Sapium Jenmani* and certain other species of *Sapium.*[8] Tall trees are characteristic of all known species.

[7a] E. Ule, *Tropenpflanzer Beihefte,* **6,** 1 (1905) and *Bot. Jahrb.,* **35,** 663 (1905); and O. Labroy and V. Cayla, "Culture et exploitation du caoutchouc au Brésil," Societe generale d'impression, Paris, **1913.**

[8] See P. Preuss. "Expedition nach Zentral-und Südamerika," p. 384, Kolonialw. Komitee, Berlin, **1901;** J. Huber, *Rev. cult. coloniales,* **10,** 137 (1902); H. Jumelle, *Ibid.,* **10,** 170 (1902); E. Ule, *Tropenpflanzer Beihefte,* **6,** 14 (1905); and J. B. Harrison and C. K. Bancroft, "Rubber Recueil," 56.

Figure 6—*Manihot glaziovii* plantation (11 years old) in Muhesa, German East Africa, during the dry season.

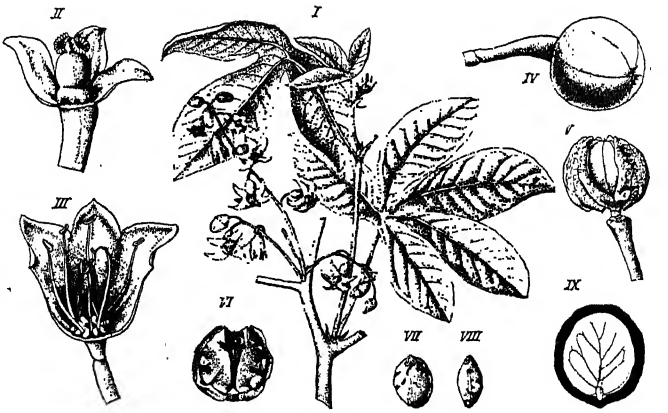


Figure 7—
Manihot glaziovii.

I. Blooming branch.
II. Female blossom.
III. Male blossom.
IV. Fruit while still green.
V. Fruit when dried out.
VI. Opened fruit compartment, seen from the inside.
VII. and VIII. Seeds.
IX. Cross section of seed.

There is a nectary on both sides at the end of the leaf-stalks. The very plain male and female flowers are united to form spikes or clusters.

"Mistletoe" Rubber. This rubber was much discussed at the time when prices were low. It was obtained from the fruit of certain *Loranthaceae* which occur as parasites on the coffee tree, and was designated as "Thina-Rubber." Commercially this rubber seems never to have played any noteworthy role.[9]

Central America and Mexico

Most of the rubber from Central America is obtained from the various species of *Castilloa*—the *Castilloa panamensis* of Panama, the *Castilloa costaricana* and *Castilloa micoyensis* of Costa Rica, and the *Castilloa elastica* (Fig. 3) and *Castilloa lactiflua* of Mexico. Certain other species, which yield rubber of smaller value, are also to be found in Central America.[10]

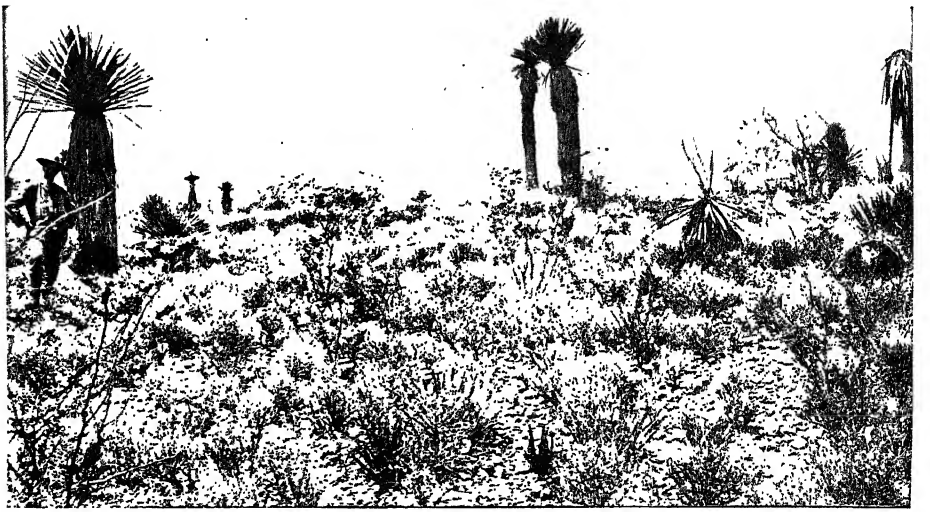


Figure 8—Guayule plants on the deserts of northern Mexico.
(Courtesy of F. E. Lloyd.)

In the arid regions of southern Mexico, rubber is harvested from the Guayule plant (*Parthenium argentatum*), which belongs to the Compositae family.[11] (*See* Figs. 8 and 9.) Large plains in this district are almost completely covered by the Guayule shrub. The rubber is recovered from these plants by extraction or by mechanical methods. When the price of rubber is high, Guayule rubber is put on the market in considerable quantities. The export from Mexico amounted to 8,946 tons in the year 1910-1911, for instance. When the price of rubber went down, the production of Guayule became negligible. In 1926 it increased again to 4,306 tons.*

[9] O. Warburg, *Tropenpflanzer*, **9**, 633 (1905); H. Iltis, *Sitzber. Akad. Wiss. Wien, Mathem.-naturw. Klasse*, **120**, 217 (1911).

[10] O. F. Cook, *U. S. Dept. Agr., Bur. Plant Ind., Bull.* **No. 49**, (1903); H. J. Pittier, *Contrib. from the U. S. Nat. Herbarium*, **13**, 247 (1910).

[11] See F. E. Lloyd, "Guayule," *Carnegie Institution Publication* **No. 139** (1911).

* Translator's Note. According to information furnished by the United States Department of Commerce, the imports of Mexican Guayule rubber into the United States increased from 4,306 tons in 1926 to 5,018 tons in 1927, and then decreased steadily to a negligible quantity in 1931. V.N.M.

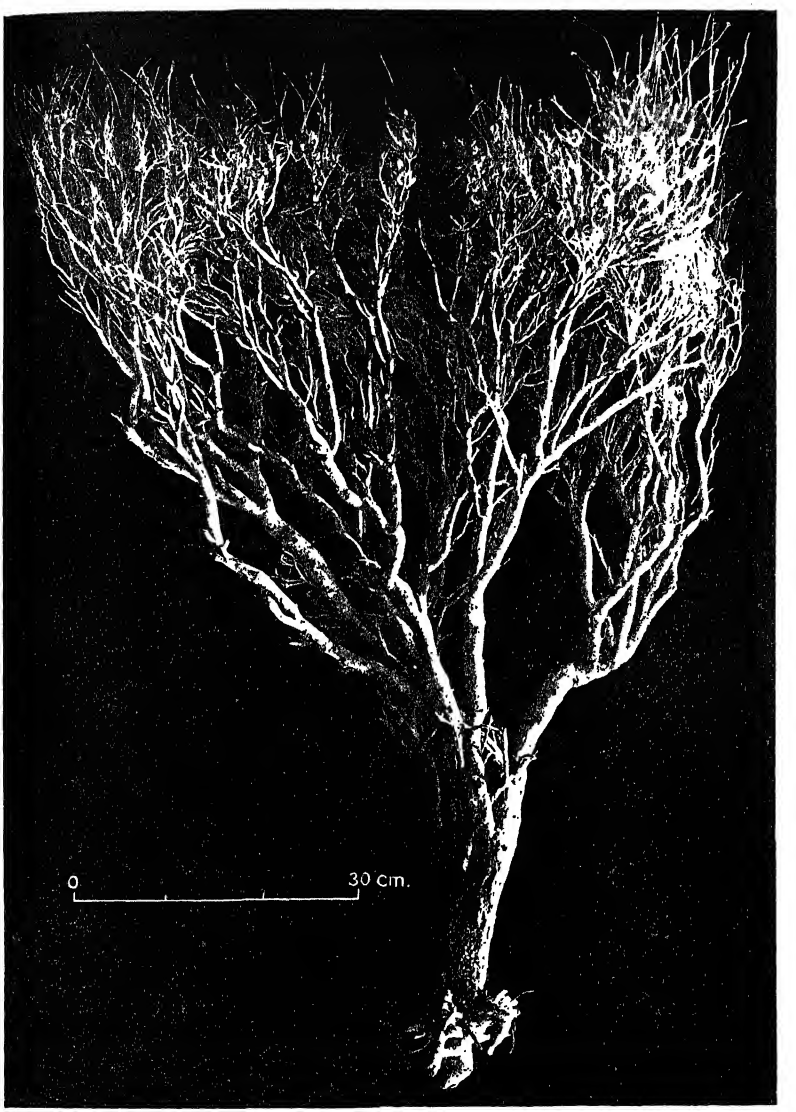


Figure 9—An exceptionally tall Guayule plant. (Courtesy of F. E. Lloyd.)

Rubber known commercially as "Palao amarillo" is also obtained in Mexico from the *Euphorbia fulva.* This rubber contains a high proportion of resins.

In Central America, there is also obtained from the *Achras Sapota* a substance which is used for the preparation of the so-called "Chicle gum."

United States of America

At the time of the World War the investigation of a large number of latex-yielding plants was begun in the United States of America. It was hoped to

discover one which would be suitable for the profitable production of rubber. In the dry districts of certain western states were found shrubs (species of *Chrysothamnus* and *Haplopappus* especially) from which rubber could be obtained in a manner similar to that used for recovering Guayule rubber.[12] The possibility of harvesting the existing stands, or of cultivation on a profitable basis in peace times, should not be overlooked. Fairly successful attempts to increase the rubber content by rational breeding have been made. That the mechanical production of rubber may become relatively cheap does not seem impossible in these days of the high cost of labor. It is of interest to mention, furthermore, that many of these species thrive on dry and poor soils which are unsuitable for the production of other crops. Experiments along this line have been carried on more recently in Florida by Thomas A. Edison. He is said to have investigated over 3,000 plants as possible sources of rubber, and to have obtained promising results.

Goldenrod is one of the common plants which have recently received attention.* According to L. G. Polhamus [*J. Agr. Research,* **47,** 149 (1933)], the leaves of 24 species of goldenrod were found to have rubber contents varying from 0.56 to 6.34 per cent. The variation in the rubber content within certain of the high-yielding species indicates the possibility that plant selection and proper cultural practices might lead to strains with higher rubber content.

J. C. Wichmann[13] is also said to have succeeded in obtaining from the sap of the *Opuntia,* which grows wild in America, a rubber-like substance, which is said to be a possible substitute for rubber.

Africa

For a long time Africa has held second place among the continents which produce wild rubber. In the year 1900, the exports of rubber from Africa amounted to about 16,000 tons, while those from the ports of the Amazon were about 27,000 tons. The total world production of that year was 50,000 tons. According to H. N. Whitford and A. Anthony[14], the maximum African production, 20,500 tons, occurred in 1906. A gradual decrease took place thereafter, a minimum of 2,433 tons being reported in 1922.†

The quantities of rubber produced in the individual countries of Africa have fluctuated considerably from year to year. This fluctuation is attributed in part to the irrational tapping procedure of the natives, which frequently leads to the destruction of existing trees. Political situations and the other means of livelihood open to the natives are other factors which have influenced production. The maxima in rubber production for the different countries fall consequently in different years, as is apparent from Table 1.

TABLE 1.—*Maximum Production.*

Country‡	Year	Quantity (tons)
Belgian Congo	1901	5,954
Angola	1904	3,186
French Equatorial Africa	1917	2,948
Cameroons	1913	2,832
Gold Coast	1898	2,672
French Guinea	1912	2,008
Nigeria	1906	1,533
Senegal	1910	1,533
Ivory Coast	1904	1,512
Madagascar	1906	1,247

‡ Districts producing less than 1,000 tons not included.

[12] H. M. Hall and T. H. Goodspeed. *Univ. California Publ. in Botany,* **7,** 159 (1919).
[13] *India Cultures,* **13,** 558 (1928).
[14] *U. S. Dept. Commerce, Trade Promotion Series,* **34,** 8 (1926).

* Translator's note by V. N. M.
† Translator's Note. Fluctuating with the price of rubber, the African exports were up to 8,410 tons in 1927 and down to 1,747 tons in 1932. V.N.M.

In contrast to the American wild rubber, which is obtained almost exclusively from rather large trees, the wild rubber of African origin is derived largely from lianas (vines). These plants exhibit, when young, a shrub-like growth. After reaching a certain age, however, they put out long shoots having stalks so weak that they do not appear to be able to stand upright without support. Like our pea or cucumber plants, they are provided with numerous branched tendrils, which stretch out in all directions. When these tendrils come in contact with a suitable support, such as the branch of a tree, they fasten around the latter tightly. (*See* Fig. 10). By this means, it is possible for the liana, despite its weak stem, to climb to the very top

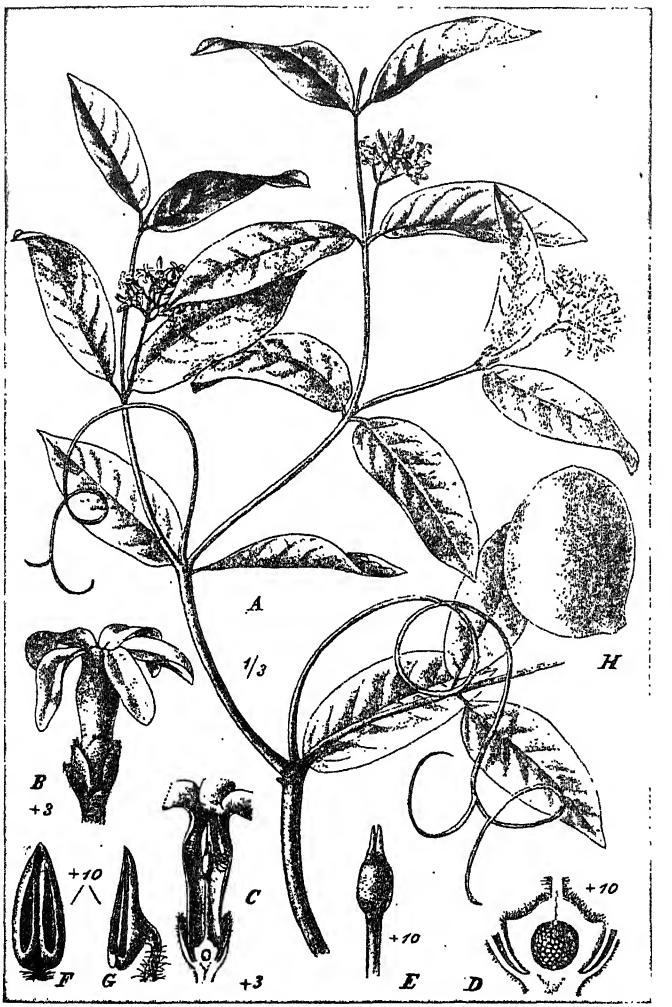


Figure 10—*Landolphia Heudelotii* (Courtesy of R. Schlechter). A. Branch. B. Flower. C. Flower, cut lengthwise. D. Ovary, cut lengthwise. E. Head of style. F. Anther (front view). G. Anther (side view). H. Fruit.

of tall trees and produce its flowers and fruit in their crowns. The stalks of the older rubber lianas may attain a length of 20 meters or more and a circumference at the base of 10 to 20 cm.

The African liana (vine) rubber is now derived largely from various species of the closely related genera, *Landolphia* and *Clitandra*. The different kinds are not graded commercially according to their origin, however, but rather according to the land where produced, the harbor from which exported, or the method by which produced. Since distinguishing the various species is difficult even for an expert, and varieties of the same species seem to produce rubbers of differing quality, it is easily understandable that a decision regarding the botanical origin of the different commercial kinds of vine rubber cannot be made with any assurance. In tropical western Africa good rubber is obtained especially from the *Landolphia Heudelotii* of the northern districts, and from the *Landolphia owariensis* of the southern. In eastern Africa the chief source is *Landolphia Kirkii,* of which there are several varieties. Satisfactory rubber is also obtained from the *Clitandra elastica* and *Clitandra laurifolia* of the Ivory Coast region; the *Carpodinus landolphioides, C. uniflora* and *Cl. Simoni* of Cameroons; *the Cl. nzunde, Cl. orientalis* ("Noir du Congo" or "Black Congo"), *Landolphia Gentilii* ("Rouge de Kassai" or "Red Kassai"), *L. Klainei, L. Droogmansiana, Oncinotis hirta* and *Periploca canariensis* of Belgian Congo; the *L. parvifolia* ("Muteke") of Rhodesia; the *L. kilimandjarica, L. Petersiana, L. Stolzii* and *Holarrhena microteranthera ("Piripiri")* of German East Africa (Tanganyika Territory); the *L. Watsoniana* of British East Africa and the *L. Dawei* and *L. ugandensis* of Uganda.

Of primary importance among African trees is *Kickxia elastica* (also called *Funtumia elastica*). (*See* Fig. 11). The territory in which this tree grows reaches from Lagos to Lake Victoria. The rubber obtained from it comes into the market under the designation of "Silk Rubber." *Ficus Vogelii,* which grows rather extensively in western Africa, yields a rubber of average quality. Good rubber is also said to be obtainable from the *Ficus Preussii* of Cameroons and the *Ficus nekbudu* and *F. bubu* of Belgian Congo.

"Mgoa Rubber" is the commercial name of the rubber from *Mascarenhasia elastica,* which is to be found in the form of small trees in damp, low places and along the rivers of the east coast of Africa, especially German East Africa. *Euphorbia rhipsaloides* yields a rubber very rich in resin. This rubber, which is produced in Angola, is known commercially as "Almeidina" or "Potato Rubber." When rubber was high in price, a product with a very high resin content was brought into the market from Natal. This rubber was obtained from *Euphorbia Tirucalli* (Fig. 12). In southern Africa efforts have recently again been made to procure rubber from the cactaceous species of *Euphorbia,* which form trees up to 10 meters in height. According to E. Neufeld,[15] *Euphorbia grandidens, E. tetragona,* and *E. triangularis* are satisfactory for this purpose. These species yield products containing considerable resin and only about 25 per cent rubber. Like Guayule rubber they can be used to advantage when mixed with other kinds of rubber. Moreover, it is possible to separate resin and rubber, and to make subsequent use of each constituent. There appears, however, to have been no appreciable production of Euphorbia rubber so far. W. Spoon and M. van Royan[16] have questioned the profits to be expected from efforts expended in this direction.

[15] *Kautschuk,* **3,** 359 (1927).

[16] *Ind. Merc.,* **50,** 209 (1927) and **51,** 195 (1928).

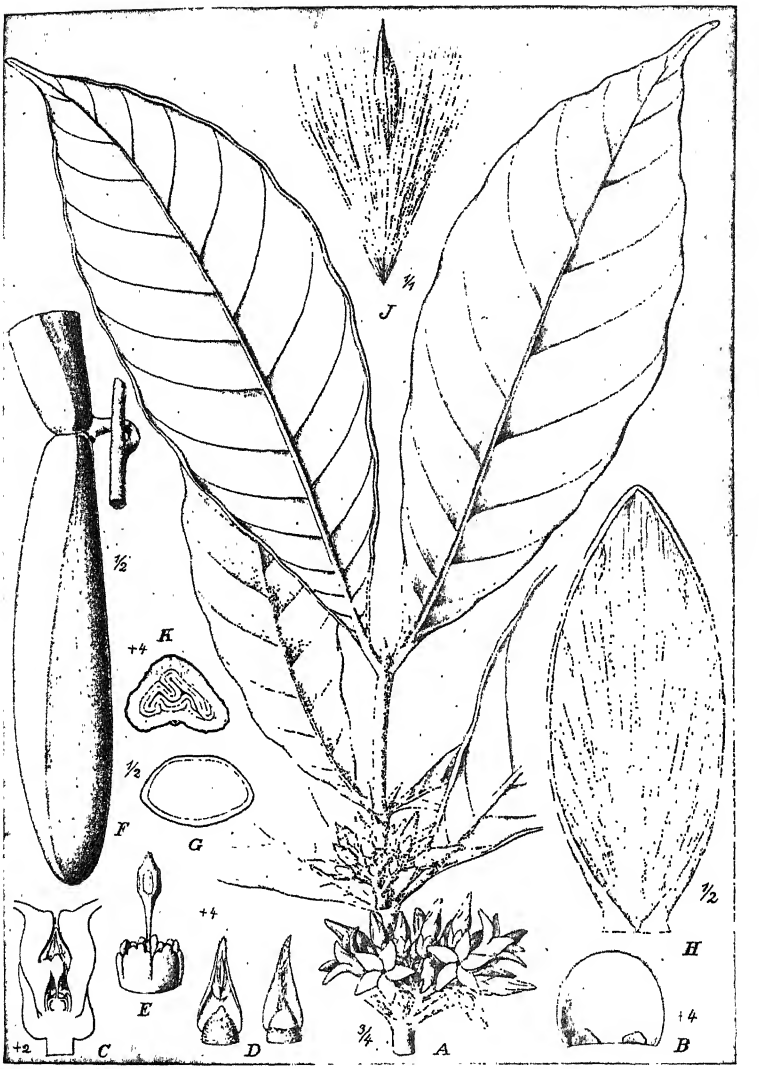


Figure 11—*Kickxia elastica* (Courtesy of R. Schlechter). A. Blooming branch. B. Sepal. C. Flower, cut lengthwise. D. Anthers. E. Ovary with style. F. Fruit. G. Fruit, cut transversely. H. Half of fruit, opened up. J. Seed. K. Transverse section of seed.

In addition to the rubber obtained from vines and trees, the so-called root or herb rubber plays a certain role in Africa. This latter is obtained by mechanical means from low bushes, which are too small in size to permit of profitable tapping. (*See* page 65.) A considerable portion of the rubber obtained comes from the extensive root systems of these plants. The most important source of root rubber seems to be *Landolphia Thollonii*. Some rubber is also said to be obtained from certain species of *Carpodinus* (Figs. 13 and 14).

Figure 12—*Euphorbia Tirucalli* in the steppes near Makauga (German East Africa).

It should also be mentioned that in Angola, rubber has likewise been obtained from the shrub-like *Raphionacme utilis*, and has been exported under the name of "Ekanda Rubber."

The island of Madagascar is characterized by the great abundance of rubber-producing plants. As on the African continent, those belonging to the genus *Landolphia* are the most important. Of the 14 species of *Landolphia* already known, part yield good rubber and part less usable rubber. The most widely distributed species appears to be *Landolphia Perrieri* ("Piralahy"), which yields rubber whose usual commercial designation is "Majunga Noir." Good rubber is furthermore obtained from *Landolphia sphaerocarpa* ("Reiabo"), *L. crassipes* ("Fingotra"), *L. fingimena* and *L. hispidula.* Among other rubber-producing plants, mention may also be made of *Cryptostegia madagascariensis* ("Lonbiro"), *Secamonopsis madagascariensis* ("Vahimainty") and *Gonocrypta Grevei* ("Kompitso").

Mascarenhasia arborescens ("Guidroa"), which is the source of part of the "Majunga Noir," deserves first mention among the trees yielding rubber

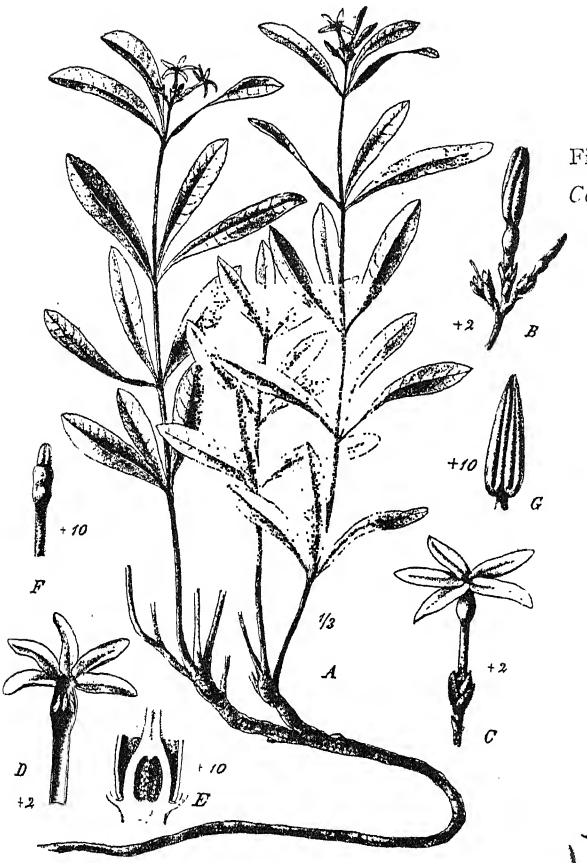


Figure 13—
Carpodinus lanceolatus.

A. Characteristic form of plant.
B. Buds.
C. Flower.
D. Flower, cut longitudinally.
E. Longitudinal section of ovary.
F. Top of the style.
G. Anther.

(Courtesy of R. Schlechter.)

Figure 14—*Carpodinus chlorrhiza.*
(Courtesy of H. Baum.)

in Madagascar. Good rubber is also obtained from the *Mascarenhasia lisianthiflora, M. lanceolata, M. mangorensis,* and to some extent from certain other species of *Mascarenhasia.* Considerable rubber was formerly derived from *Euphorbia intisy* ("Intisy" or "Herotra"). This species is now almost completely exterminated, however. The same also applies to *Euphorbia pirahazo,* which never produced any great quantity of rubber.[17]

[17] *Cf.* especially Jumelle, H. J., "Les plantes à caoutchouc et à gutta," Paris, 1903; "Rubber Recueil," p. 38.

Asia and Polynesia

The quantity of wild rubber produced in Asia has been relatively small in comparison to that obtained from the Americas and Africa, although there have been temporary exports of some consequence, especially from India (proper) and Burma. In 1872-73, for instance, these amounted to 1,095 tons. Again, 1,288 tons were exported from Singapore in 1897.

First to be discussed among the Asiatic sources of wild rubber is *Ficus clastica* ("Karet," "Rambong"), which is also grown considerably in Germany as a house plant, under the name of "Gummibaum." In the tropics, this species forms very large trees (Figs. 15 and 16), the roots of which start above ground. At the point where it penetrates the ground a root of

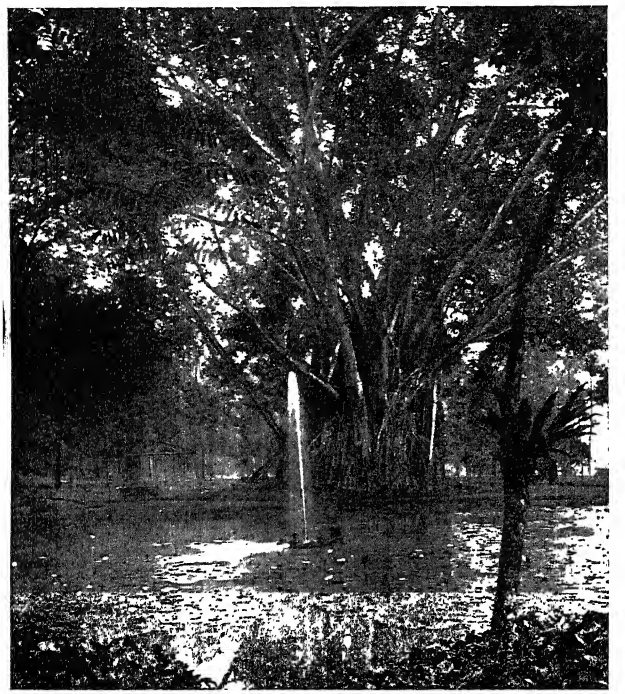


Figure 15—*Ficus elastica* in the botanical gardens at Buitenzorg (Java).

this tree may have a thickness as great as that of a man's thigh. *Ficus clastica* is distributed over a territory extending from south of the Himalayas to the Sunda Islands. Considerable quantities of good liana (vine) rubber are also obtained from Asia. The source of this rubber is particularly the *Willughbya firma* of the Sunda Islands. Good rubber is produced, moreover, by the different species of *Urceola,* which likewise grow in the form of vines. Among these may be mentioned *Urceola clastica* (of primary importance), *U. brachysepala, U. esculenta* (Rangoon), *U. acutoacuminata* ("Serapat"), *U. malaccensis* (Malacca), *U. Maingayi* (Malay Archipelago) and *U. pilosa* (Borneo).*

Translator's Note. According to recent reports, the tau-sagyz plant (a species of *Scorzonera*), which is indigenous to the mountains of Kazakstan in Soviet Russia, has been found to yield rubber of good quality. See G. H. Carnahan, [*India Rubber World,* **85,** No. 5, 93 (1932)] and U. S. Dept. Commerce, Bur. Foreign and Domestic Commerce, Special Circ. Nos. 3313 and 3359 (1932). V. N. M.

A rubber of less value, which is marketed under the names of jelutong, "Dead Borneo," and pontianak, is derived chiefly from the different species of *Dyera*, especially *Dyera costulata* and *D. Lowii*. These two species, which are widely distributed in Borneo, form trees of great size. The various species of *Alstonia* constitute another source of this rubber.

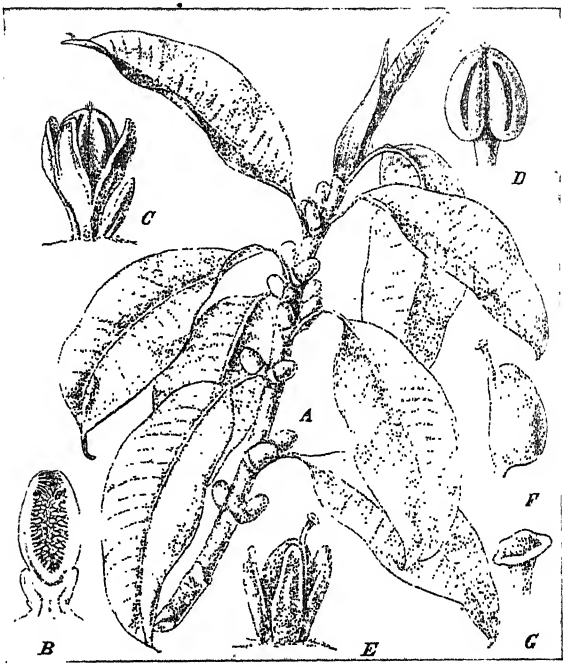


Figure 16—

Ficus elastica

A. Branch with inflorescences.
B. Syncarpy, cut longitudinally.
C. Male flower.
D. Stamen.
E. Female flower.
F. Ovary.
G. Stigma.

(Courtesy of O. Warburg.)

In Burma there are also to be found three rubber vines; *viz.*, *Ecdysanthera mikrantha, Parameria barbata* and *Rhynchodia Wallichii*. In French Indo China the lianas include *Ecdysanthera cambodiensis, E. Godefroyana, E. linearicarpa, E. Quintareti, E. Tournieri, Micrechites Bailloni, M. napeensis, Parabarium diudo, Xylinbaria Reynaudi,* and the tree-like *Bleekrodia tonkinensis*. Other Asiatic vines containing rubber are the *Parameria philippinensis* of the Philippines, the *Ficus hypophaea, F. Supfiana,* and *Ichnocarpus xanthogalax* of Dutch New Guinea, the *Ficus rigo* of British Guinea and the *Alstonia Dürkheimiana* and *Ficus Schlechteri* of New Caledonia.

Although gutta-percha* need not necessarily be discussed in a treatise on rubber, the two substances are so frequently associated that mention of the botanical sources of the former seems not to be out of place. Gutta-percha is obtained from various trees of the Sapotaceae family, particularly those of the species *Palaquium* (also called *Dichopsis* or *Isonandra*) *oblongifolium* and *Palaquium obovatum*. The commercial product comes chiefly from Southeastern Asia and islands off the coast of Asia; Singapore being the main shipping point. (See *Bur. Standards, Circ.* **No. 38**, 5th ed., p. 11, 1927; Clouth, F., "Rubber, Gutta-percha and Balata," D. Van Nostrand Co., New York, **1903**; and Fischer, E. J., "Guttapercha und Balata," Allgemeiner-Industrie Verlag, Berlin, **1933**.

* Translator's Note by V.N.M.

Plantation Rubber

The first attempt to establish a plantation for the express purpose of obtaining rubber was made in Java. A small planting of *Ficus elastica* was undertaken by the Forest Administration of that territory in 1861. Three years later, more extensive plantings of this rubber tree were made in the Tjiasem and Pamanoekan lands of West Java. These constitute the first rubber plantations in the world. The exports of rubber from them in 1894 amounted to 3.1 tons. Experiments with other rubber plants were later conducted by the various tropical botanical institutes. Rubber trees were also planted upon many private estates, principally for the purpose of providing crops of secondary importance. From the beginning of the present century, the increasing consumption of rubber and the consequent higher price has led to a steady increase in the extent of the cultivation of rubber trees. Although experiments were formerly conducted with various species of rubber-producing plants, it has gradually become more and more apparent that *Hevea brasiliensis* is the most suitable species for districts having climate and soil favorable to its growth. The cultivation of *Hevea* on the plantations is consequently given first attention below. Experiments carried out with other species are subsequently discussed.

Hevea

Information regarding the vast expansion in the cultivation of *Hevea* is presented in Table 2, which lists the areas covered by *Hevea* plantations in 1926 (statement by the Rubber Growers' Association).

In view of the important role which the *Hevea* plantations play in the production of rubber, certain details of general interest in connection with the arrangement of the plantations and the work carried out on them will be presented below. Any readers who desire to enter the business of the cultivation of *Hevea* are referred to the special literature on the subject.[18]

Table 2.—*Total Area Planted in Hevea.*

	In 1,000 acres	In per cent of the total area
Malaya	2,250	47.4
Netherlands East Indies	1,600	33.6
Ceylon	450	9.5
Borneo and Sarawak	150	3.1
India	140	3.0
French Indo China	90	1.9
Other Countries	70	1.5
Total	4,750	

The first consideration in connection with the selection of the district for a plantation is that *Hevea brasiliensis* thrives best in a damp, warm climate. Although some success may be had with this species in a rather dry climate, its growth is considerably slower and the yield much smaller than when it is grown in districts having a damp climate. In general, the planting of *Hevea* can only be recommended for such districts as have a rainfall of at least 2 meters per annum. From the standpoint of temperature, furthermore, it is not desirable to go too far up into the mountains. In the tropics, land having an elevation not over 500 meters above sea level is best suited for the cultivation of *Hevea*. The growth of the tree is nat-

[18] See Wright, H., "Hevea Brasiliensis or Para Rubber; its Botany, Cultivation, Chemistry and Diseases," 4th ed., Maclaren & Sons, 1912; Lock, R. H., "Rubber and Rubber Planting," University Press, 1913; and Swart and Rutgers, "Handboek voor de rubbercultuur in Nederlandsch-Indië," J. H. De Bussy, 1921.

urally also dependent upon the nature of the soil. A deep, virgin forest soil, rich in humus, and having a ground water level which is not too high, is the most favorable. Boggy country requires thorough draining. It should be borne in mind that the roots of *Hevea* trees penetrate loose soil to a depth of 3 to 4.5 meters, and sometimes even farther.

The propagation of the plants is carried out almost exclusively from seeds, which begin to germinate a few days after being planted. They lose their ability to germinate rather quickly—within about two months when satisfactorily preserved, and often in even less time. The preferred procedure consequently is to plant them as soon as possible after they have been harvested.

In connection with the selection of stock it might first be mentioned that by far the greater part of the trees in the Middle East originated from seeds collected in Brazil by H. A. Wickham in 1876 and planted in Kew Gardens in London. The seedlings raised from these seeds were sent to Ceylon and Singapore and became the mother plants for almost all of the *Hevea* planted in the Middle East and in Africa. These plants are obviously all of one species, *Hevea brasiliensis*. They are, however, of many varieties or types, differing in morphological properties and especially in yield-capacity. As a consequence, trees growing under the same external conditions and tapped in the same manner, may be capable of yielding quite different quantities of rubber. This is illustrated in the following table, which presents the results of tapping experiments made by Schierke.[19] A total of 6,165 trees (approximately 10 years old) was tapped, and groupings were made in accordance with the quantity of rubber produced.

TABLE 3.—*Yield of Hevea Trees Growing under the Same Conditions.*

Yield per tree in each group in grams	Number of trees in each group	Production of each group in grams	No. of trees in each group in % of the total number	Production of each group in % of total production
1 to 10	2,678	5,812	43	19
11 to 20	2,006	7,456	33	24
21 to 30	703	5,651	11	19
31 to 40	360	4,033	6	13
41 to 50	216	3,125	4	10
51 to 60	72	1,246	1	4
61 to 70	40	806	0.7	3
71 to 80	43	980	0.7	3
81 to 90	24	627	0.3	2
91 to 100	17	485	0.3	2
101 to 110	---	------	---	---
111 to 120	2	69	0.03	0.2
121 to 130	4	155	0.06	0.5
Totals	6,165	30,445		

From Table 3, it is evident that the trees yielding from 21 to 130 grams produced 57 per cent of the total quantity of rubber, although they constituted but 24 per cent of the total number of trees. Furthermore, 7.1 per cent of the trees, each yielding from 41 to 130 grams of rubber, accounted for 25.5 per cent of the total production. Results agreeing with those shown above have also been obtained by other investigators.

[19] See N. L. Swart and A. L. Rutgers, "Handboek voor de rubbercultuur in Nederlandsch-Indië," p. 50, J. H. De Bussy, 1921.

Further studies have demonstrated that the specific quantitative yield-capacities of the trees are not appreciably changed by continued tapping over a long period of time. It is thus possible to distinguish in general between high- and low-yielding trees. It is the endeavor of the planter to have trees with the highest possible yield capacities distributed uniformly over his plantation. On estates already existing and usually planted too thickly, a considerable increase in capacity has been brought about by thinning out the poor-yielding trees only. By vegetative propagation—especially bud-grafting from high-yielding trees—it is also possible to obtain plantations with higher average yield capacities.* The principal effort now is to grow high-yielding seedlings by means of careful selection of seeds. Since the productive capacity cannot be determined with any certainty until the tree is several years old, considerable time and effort is expended before any decision can be made. The experiments in seed selection have nevertheless already given some promising results.[20]

It is recommended that seeds selected for planting should be collected only from trees characterized by a large size and a high yield of rubber. In practice this selection is rendered difficult by the fact that the seeds are hurled for some distance when being discarded by the trees.

The seeds may be either planted in the field or else first grown in a nursery. In the latter case, before planting in the field, the seedlings are set out in pieces of tube-shaped bamboo stalks, or in planting baskets made of the sheaths of banana leaves, pandanus leaves, etc. The larger plants are trimmed (stumped) before the final replanting. The plants in this condition, with shortened stalk and main root (so-called "stumps"), are in an especially satisfactory form for transportation over a considerable distance.

The land where the seedling is ultimately to be set out is prepared while the latter is being grown. If it is a case of virgin forest, all bushes and trees on the land are first felled (and burned in place, provided there is no other use for them). The ashes obtained are distributed uniformly over the plantation. With very damp soil, it is necessary to take care of drainage by means of ditches.

In order to make the subsequent control of the work of planting easier, the whole clearing is parceled out into square or rectangular divisions of uniform size (about 1 hectare). The boundaries of the divisions or fields can also serve as roads, in case the land is relatively level. In mountainous country a more carefully planned network of paths (roads) must be laid out.

After the ground has been prepared in this manner, the places where the plants are to be set out are marked. The locations for the plants are usually arranged in rows parallel to the borders of the individual divisions in such a manner that the distance between trees in a row is the same as the distance between rows. This distance between plants was formerly quite small—often about three meters, for instance. Greater distances have gradually come into vogue. Although the planting of fewer trees per acre results in a smaller yield in the early years, this difference is soon overcome as a consequence of the greater development of the less densely planted trees. More-

* Translator's Note. According to C. H. Wright ("Modern Aspects of Rubber Cultivation," p. 118, Maclaren & Sons, London, **1928**), "A yield of 1,250 pounds of rubber per annum from a mature field of budded trees, at 10 to 15 years old, may probably be taken as a safe figure as compa ordinary unselected seed."

[20] See *Tropenpflanzer*, **30**, 268 (1927).

over, the vitality of the trees is greater and the cost of tapping is considerably less in the case of trees planted farther apart. Distances as great as 10 meters have recently been recommended. Use is also often made of the method in which the plants are set out rather close together and the distance necessary for fullest development is later obtained by means of selective "thinning out."

In order to facilitate the growth of the young plant, a hole is dug at the place where it is later to be planted. This hole may be cubical in shape, each dimension being about 0.5 meter. Some time before the actual planting, the hole is again filled in.

In former years, the ground was generally freed from weeds before planting (clean weeding), especially in the English colonies. The conviction has gradually been reached, however, that the resulting continuous exposure of the soil to the sun has a disadvantageous effect on its chemical and physical properties, and on the microörganisms contained in it. Recently, there has been considerable tendency to plant cover crops (green manuring) and thus not only shade the soil but also enrich it by adding nitrogen and humus.† Where the country is very hilly, the erosion of the top soil is disadvantageous. Attempts have been made to increase the development, and especially the yield, of rubber trees by using chemical fertilizers. With poor, exhausted and badly eroded soils very favorable results have often been obtained by using fertilizers. M. K. Bamber[21] observed an increase in the yield of rubber when using fertilizers, especially those containing nitrogen and phosphorus. Lime is also recommended, although care is required in its use. The experiments along this line cannot yet be said to have led to conclusive results.*

In order to obtain returns from the plantations in the first few years, other crops (intercrops) are often grown between the *Hevea* trees. Annual plants, such as maize, maniok, tobacco, sesame, and peanuts, are in favor for this purpose. Plants of longer life, such as cacao and coffee, are also often planted among the rubber trees on plantations. In recent years the preference has been for Robusta coffee, which produces a large crop at an early date. In the first few years, a certain amount of shade seems to be demanded by the *Hevea* trees; later, their tops must be completely exposed to the light of the sun.

As with all large stands of trees, there exists the danger that the epidemic occurrence of diseases or insect pests may destroy individual trees or whole plantations. In the various territories where *Hevea* grows, a large number of pests and diseases are already to be observed. Especial mention may be made of termites, root fungi and brown bast, which is favored by tapping too heavily.[22]

† Translator's Note. Recent tests conducted by W. B. Haines [*J. Rubber Research Inst. Malaya*, **5**, 78 (1933)] indicate that the growth of young *Hevea* trees is inhibited somewhat by cover crops, since the latter compete for the available plant food. V. N. M.

[21] *Dept. Agr. Ceylon Bull.*, **No. 36**, (1918).

* Translator's Note. Recent results have indicated that the use of fertilizers is usually advantageous, provided judgment is used with respect to the district to be fertilized and the mixture to be employed, and also with regard to the mode and time of application. Thus C. H. Wright ("Modern Aspects of Rubber Cultivation," p. 81, Maclaren & Sons, London, **1928**) states, "In the majority of cases it may reasonably be said that there are very few estates where it would not be possible to improve the growth of the rubber, and secure large crops on some area or other of the property in question, by manuring." V.N.M.

[22] See Petch, T., "The Diseases and Pests of the Rubber Tree," London, **1921**; Steinmann, A., "De ziekten en plagen van Hevea brasiliensis in Nederlandsch Indië," Archipel Drukkery, Buitenzorg, **1925**; Weir, I. R., "A Pathological Survey of the Para Rubber Trees (Hevea Brasiliensis) in the Amazon Valley," *U. S. Dept. Agr., Bur. Plant Ind., Bull.* **No. 1380** (1926).

Thus far, however, after exact studies of the diseases produced by the pests, the entomologists and mycologists at the various stations, have combated their further spread successfully. It should be mentioned nevertheless that, according to G. Stahel,[23] the occurrence of a leaf disease introduced by a fungus caused the abandonment of *Hevea* cultivation in Dutch Guiana.

The final matter to be considered at this point has to do with the cost of preparation of plantation rubber. H. E. Miller[24] reported that this amounted to about 2 shillings a pound in 1910, and 1 shilling (approximately 24 cents) in 1915. Upon well conducted plantations the "all-in" cost in 1927 was as low as 10 pence (about 20 cents) per pound. According to a compilation in Gummi-Zeitung [Vol. 41, 2373 (1927)], the average cost for 49 Dutch plantation companies was 6.45 pence per pound. The cost of preparation and delivery at the port of export amounted to 75.8 guilder cents per kilogram (about 14 U. S. cents a pound) on the rubber establishments of the Dutch Government, according to A. W. de Jong.[25] *

Manihot

The only one of the various species of *Manihot* which has been cultivated to any extent up to the present time is *Manihot Glaziovii*. The experiments already conducted make it appear that the growing of the other species would probably be unprofitable.

Since *Manihot Glaziovii* requires much less moisture than *Hevea,* and does not exhaust the fertility of the soil as rapidly as does the latter, it can be cultivated in districts which would not be suitable for profitable plantations of *Hevea*. *Manihot* thrives, for instance, in the relatively dry lowlands of German East Africa (Tanganyika Territory). In the year 1913, rubber plantations covered 45,317 hectares in this district. Of this number, only 17,116 hectares were yielding rubber. The 12,088 tons of plantation rubber harvested in this region in 1913 were derived almost exclusively from *Manihot Glaziovii*.

In contrast with *Hevea, Manihot Glaziovii* has the further advantage of yielding rubber at an early age. The trees may be tapped after two years' growth. Although trees were often tapped while even younger in German East Africa, the process was very deleterious to the vitality of the plants. In the early days, the plants were also placed too close together in the attempt to obtain the highest possible yield. The profits obtained from these plantations were nevertheless considerably less than those from the *Hevea* plantations of the Middle East. In fact it is doubtful whether plantings of *Manihot Glaziovii*, even with systematic cultivation and tapping, can ever compete with a well-situated *Hevea* plantation, since in the case of the latter the yield per acre is considerably greater and the cost of tapping appreciably less. By using systematic and uniform methods of preparation, it should be possible to decrease the difference in price between Manihot (which is capable of broad industrial application) and Hevea rubbers. It does not seem unreasonable to believe that, were it not for the overproduction of rubber for the world market, it would be possible to continue the profitable cultivation of *Manihot* in districts where the growth of *Hevea* would not pay, but where the labor situation was such as to make possible a low cost of preparation of the rubber. Like *Hevea,* but in contrast with other rubber

[23] *Bull. Dept. Landbouw Suriname,* **34,** 1 (1917).

[24] *Bull. Rubber Growers' Assoc.,* **9,** 774 (1927).

[25] *India Cultures,* **12,** 1032 (1927).

* Translator's Note. At the present time (Mar., 1933), the cost of preparation of rubber is much less, although it undoubtedly remains above the selling price (less than 4 cents per pound in New York). V.N.M.

plants, *Manihot* will produce a profitable yield of rubber over a long period during which tapping is repeated at short intervals.

The distance of 2.5 meters between plants, which is common in German East Africa, should certainly be given up in favor of distances of 4 or 5 meters. Since the trees of *Manihot Glaziovii,* like those of *Hevea brasiliensis,* exhibit wide differences in yield-capacity, even when grown under the same conditions, selective thinning and the propagation of high-yielding stock should greatly increase the profits obtainable. For a more thorough discussion of the cultivation of *Manihot,* reference to the detailed monograph of the writer is suggested.[26]

Ficus elastica

As previously mentioned, *Ficus elastica* was planted on the first rubber plantation. Since this species is indigenous to the East Indies and the Malay Archipelago, it is only natural that it was used in the first cultivation experiments in the Old World. *Ficus* was later replaced more and more by *Hevea* and *Manihot,* primarily because of the long time required for it to come into production and the relatively low yield per acre and per year which were obtained. Experiments carried out at various places in the tropics have indicated that a *Ficus* tree produces a large quantity of rubber when first tapped, but rapidly decreasing quantities upon being repeatedly tapped. A long rest period is required in order to restore the original yield-capacity. Since each tree requires considerable space if its top is to be fully developed (10 to 20 meters between trees), only a small number of trees can be grown on an acre. There are various types of *Ficus elastica,* which cannot be readily distinguished from one another by means of morphological characteristics, but which deviate widely in the quantity and quality of the rubber they produce. In this connection, it may be mentioned that descendants of rubber trees (Gummibäumen) originally imported into Germany, yield only a little rubber of low value upon being transported to the colonies; even though they cannot be distinguished botanically from tropical *Ficus elastica.*

From the discussion above, it is easy to understand why *Ficus elastica* is no longer being planted on new estates. Trees of this species have been used as shade trees on the cacao and coffee plantations. Their widely branched crowns and extensive root systems make them quite unsatisfactory for this purpose, however. The use of *Ficus elastica* trees as wind breakers was formerly recommended, since the thick foliage of these trees makes them quite capable of holding back the wind. Furthermore, the growth of this species on portions of the plantations not used for other purposes is a possibility worthy of consideration. Since the cultivation and care required by these trees is not great, and the cost of tapping per pound of rubber produced is relatively small for old trees, a certain profit may be obtained from such plantings, provided the price of rubber is not too low.

Castilloa (Castilla)

More or less extensive experiments with *Castilloa* were carried out in the Middle East in the early days of the plantation industry. The exact species used in this work is not known with certainty. The results obtained with *Castilloa* were in every case so unfavorable as compared with those with *Hevea* that the cultivation of the former has been given up entirely, and many

[26] Zimmermann, A., "Der Manihot-Kautschuk. Seine Kultur, Gewinnung und Präparation." G. Fischer, Jena, 1913.

of the previously planted trees have already been felled. In Mexico and Central America, the natural home of various species of *Castilloa,* the cultivation on plantations was begun in 1897, according to O. Preusse-Sperber.[27]

Since *Castilloa* requires approximately the same conditions (with respect to soil and climate) as *Hevea,* and the growth of the latter is much more profitable, many of the *Castilloa* plantations have already been abandoned. In addition to the low yields obtainable, *Castilloa* is placed at a further disadvantage by the fact that the wounds in the trees made by tapping heal with difficulty, and the resulting injuries frequently lead to the death of the tree. In many regions these trees are also very much infested with animal and plant pests, especially the capricorn-beetle larvae, which live in the trunks.

Kickxia

There has been considerable planting of *Kickxia elastica,* which is indigenous to Western Africa, particularly along the coast of Cameroons. Great profit was expected from these trees, since this species is capable of yielding a very satisfactory rubber, and the giant trees of the virgin forest were known to yield large quantities of latex. As was proved by H. Picht,[28] the yields on the plantations were much smaller than had been anticipated. As with *Ficus* and *Castilloa,* long rest periods are required between tappings in order to restore the original yield-capacity. Since *Kickxia,* furthermore, requires about the same climate and soil as *Hevea,* its cultivation has been given up entirely. Nevertheless, whenever the price of rubber is not too low, the working of large stands of old trees can proceed at a profit.

Lianas (Vines)

Since many vines yield rubber which is quite satisfactory for many purposes, and since the plants were often so injured in handling that complete extermination was feared, the natives in Belgian Congo were directed to grow 50 rubber trees or lianas, or 15 plants yielding root rubber, for every 100 kg. of wild rubber harvested. In 1906 some 9,500,000 plants were said to have been in existence already. The writer has no information regarding the attention which was given these plants after they had been put out. Since the conclusion subsequently reached was that the regulation regarding the planting of trees was undesirable, it was abolished.

Before the introduction of *Hevea* into Sumatra, *Willughbya firma* is said to have been planted, partly by the natives. It was tapped first after ten years, and annually thereafter. Leembruggen[29] also started a plantation with this same species in Sumatra. It was later abandoned, as it did not prove to be profitable.

Mention should also be made of a young planting of *Landolphia Stolzii* in the Lengenburg district of German East Africa, which the writer was permitted to visit. He is of the opinion that this plantation could never have been operated profitably had not abnormally cheap labor been available.

Rubber lianas do not seem to be very well suited for plantations, because they yield little rubber until they are comparatively old. Their culture is rendered more difficult, moreover, by the fact that they must be provided with trees upon which to vine. The requirements of such trees are that they be not too high nor provided with too dense a foliage, as otherwise the development of the vines will be retarded Continual pruning is also necessary

[27] *Tropenpflanzer,* **19**, 281 (1916). [28] *Ibid.,* **23**, 10 (1920). [29] *Teysmannia,* **10**, 353 (1899).

with lianas in order to prevent them from growing together so densely as to make satisfactory tapping impossible. In fact, quicker profits would probably be derived from the cultivation of vines if they were not tapped in the regular manner, but were cut down entirely at times, and the rubber extracted from the bark by machinery. Since the capacity of these vines for regeneration is very great, rubber could again be harvested from the same stocks in a few years.

Parthenium Argentatum

Upon the experimental plantation at Salinas, California, experiments on the cultivation and acclimatization of the Guayule plant *(Parthenium argentatum)* have been in progress for 15 years. The results have been favorable, since high yields have been obtained from plants grown from selected seeds.[30]

After further experiments had demonstrated that a usable rubber could be produced from these plants, large areas in the southwestern part of the United States were planted by the Intercontinental Rubber Company of New York. Further expansion of these Guayule plantations is contemplated. The cost of production of this rubber is reported to be relatively small, since hand labor in the planting and harvesting of the rubber has been replaced almost entirely by machine operations. It is said that the Guayule rubber produced by a well-paid farmer or machinist is as large in amount as the *Hevea* rubber turned out by 15 coolies in Malaya.[31]

Cryptostegia

Experiments on the cultivation of *Cryptostegia* have been conducted in Florida and the Bahama Islands. According to an article by C. S. Dolley,[32] *Cryptostegia grandiflora* and *Cryptostegia madagascariensis* are the species which had been planted up to 1927. The prospects of cultivating these species at a profit in the United States were not considered by Dolley to be very good.

Scorzonera

Recent reports* indicate that the tau-sagyz plant, which is said to be a species of *Scorzonera,* is being cultivated in Soviet Russia. (*See U. S. Dept. Commerce, Bur. Foreign and Domestic Commerce, Special Circ.* **Nos. 3313** and **3359** (1932)]. Experiments with this plant, the roots of which contain rubber of good quality, indicate that it can be grown successfully not only in Asiatic Russia but also as far north as Moscow in Europe.

Gutta-Percha

According to Hauser,* gutta-percha has been produced on plantations in recent years. The success thus far reported leads to the belief that the cultivation of trees from which gutta-percha may be obtained will increase in the future. *See* Hauser, E. A., "Latex," (English translation by W. J. Kelly), p. 50, Chemical Catalog Co., Inc., New York, **1930.** For details, see *India Rubber J.,* **84,** 658 (1932).

[30] See V. Sauchelli, *India Rubber World,* **75,** 67 (1926); D. Spence, *Ind. Eng. Chem.,* **22,** 384 (1930).

[31] See *India Rubber World,* **79,** No. 1, 53 (1928).

[32] *India Rubber World,* **76,** 3 (1927). Also see U. S. Dept. Agr. Yearbook Separates Nos. 993 (1927) and 1299 (1932).

* Translator's note by V. N. M.

Anatomy of the Laticiferous Elements

Microscopic investigations of the laticiferous systems of various plants have demonstrated that the latex can occur in "cells," "tubes," and "vessels."

The latex "cells" differ only slightly in size and shape from the cells of the other tissue of the plant in which they are distributed. Among the rubber plants, latex cells are to be found especially in *Parthenium argentatum,* from which Guayule rubber is obtained. Since there is no connection between the individual cells, latex can flow only from such cells as have been actually opened by a cutting operation. Consequently, it is not possible to obtain the latex by tapping, as is the case with plants provided with latex tubes or vessels.

In the case of latex "tubes," such as are encountered in the rubber lianas, in the various species of *Castilloa,* and in *Ficus elastica,* a continuous tube system runs all the way through the body of the plant. The individual cells, by continuous branching, form a network throughout the other tissue present. Although there is a separation between the nuclei contained in the cells, the tubes are open and non-articulated. A movement of latex throughout the whole tube system is thus possible, and large quantities of latex can be obtained from the tubes opened when a plant of this kind is cut.

Opening a single laticiferous element by tapping also permits the removal of latex from connected elements, in the case of the "vessel" (laticiferous duct) system.* In this system, however, the latex channels result from the complete or partial absorption of the transverse walls between cells, and the simultaneous partial absorption of the lateral walls between rows of cells.

"Vessels" are to be found in the most important rubber plants, such as the species of *Hevea* which yields Para rubber, and *Manihot Glaziovii,* which is the source of Ceara rubber. Therefore, it would seem to be of interest to go somewhat more extensively into the anatomy of these plants, which seem to resemble each other markedly. The discussion will be limited to the bark, which is the only part of practical importance in connection with the collection of rubber. It should be mentioned, however, that these plants contain latex vessels in all other parts except the wood. Vessels are to be found in the pith of young stems, in the leaves and petioles, in the various parts of the flowers and in the fruit.

In Figure 17 is shown a transverse section of bark from the trunk of a young *Manihot Glaziovii* tree. It is to be observed that the vessels, which are indicated in the diagram by means of heavier lines inclosing dotted areas, form bands *(M-M)* running parallel with the cambium *(C-C).* These bands are interrupted only by the medullary rays. The diagram of the anatomy of the bark (Fig. 18) and that of the longitudinal section (Fig. 19) prove that this apparent interruption is an illusion, and that the medullary rays merely form holes through the vessel system, which latter, like the cambium, forms cylindrical layers extending along the trunk of the plant.

In that portion of bark shown in Figure 17, three cylindrical layers (rings) of laticiferous ducts are to be found. It is not difficult to understand how an increase in the number of these rings accompanies the increase in the thickness of the bark as the plant grows older. New cylinders or rings are formed by

* Translator's Note. There is considerable confusion with respect to the terminology relating to this important system. The laticifers in *Hevea brasiliensis* have been designated as "vessels," "sacs," "tubes," "ducts," "fused cells," etc. The term "laticiferous (or lactiferous) duct," implying a continuous tube or vessel formed by a row of elongated cells which have lost their intervening partitions, appears to be peculiarly appropriate. V.N.M.

adding sieve-tubes, accompanying cells, and bark parenchyma, alternately from the cambium out. In the case of *Hevea*, about three new rings are ordinarily added each year, according to P. E. Keuchenius.[33]

As soon as the trees have attained a certain age, it can be observed that the oldest rings, which lie nearest the outside, are torn apart more and more as the bark grows in thickness. They finally degenerate to such an extent that they give no latex upon being tapped.

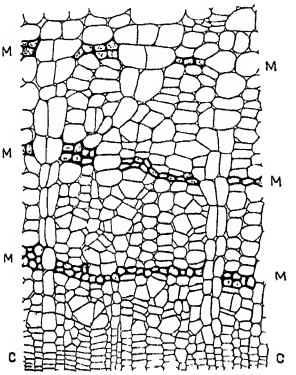


Figure 17 — Transverse section through the inner bark of the *Manihot Glaziovii*.
M-M. Latex vessels.
C-C. Cambium.

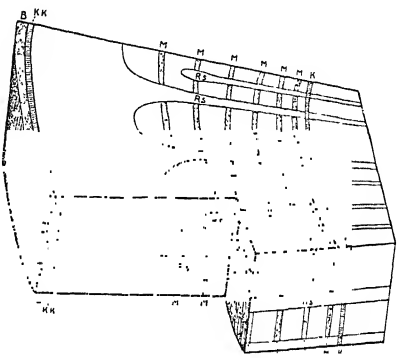


Figure 18—Diagram of the latex vessel system in the bark. K. Cambium.
M. Latex vessel system.
Rs. Medullary rays.
KK. Cork cambium.
B. Cork layer.

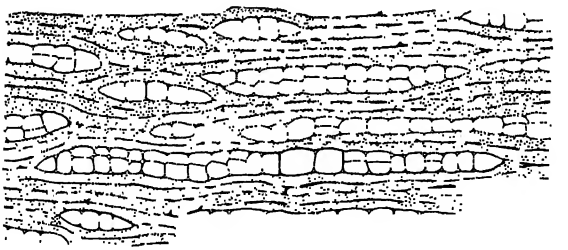


Figure 19—Tangential longitudinal section through a layer of latex vessels. (Horizontal in this diagram corresponds to vertical in the growing tree.)

Since the cambium, which lies between the wood and the bark, forms a connecting layer throughout the whole plant, from the finest root to the smallest branch, it is easy to understand how a row of latex vessels, which is first formed from the cambium, can also be continuous through the entire plant. At the base of the leaf-stem there is a partial break in the continuity of the vessels, according to W. Bobilioff.*[34] W. A. Arisz[35] has observed a similar interruption at the bases of young branches.

[33] *Arch. Rubbercultuur*, **2**, 407 (1918).
* Translator's Note. According to C. E. T. Mann, there is little or no connection between the latex vessel system of the leaf and that of the stem to which it is attached. See *India Rubber J.*, **84**, 653 (1932). V.N.M.
[34] *Arch. Rubbercultuur*, **2**, 735 (1918).
[35] *Ibid.*, **3**, 139 (1919).

Although it was formerly believed that there was no connection between the various individual rings, it has since been demonstrated by Arisz and by L. E. Cambell and G. Bryce[36] that isolated connecting links exist. These connections consist either of individual vessels or combinations of the same; or may result from forking of the ring. According to P. E. Keuchenius,[37] forking is especially to be found in the renewed bark on tapping cuts. It is stated by W. Bobilioff[38] that the number of connections between rings is usually very small, although it may be large with certain trees.

In every case, the communication established by the connecting links is quite incomplete. Consequently, upon cutting into one cylinder only the latex contained in it comes out at first; and the flow from the adjacent cylinder can follow but slowly. In fact, the yield of latex from a cut varies with the number of rings cut or with the depth of the cut in the bark. The maximum flow is obtained when the cut is so close to the cambium that latex can be delivered from all of the rings. It must be borne in mind, however, that any injury of the cambium is particularly harmful to the tree.

From Figure 19 it is obvious that the flow of latex in the longitudinal direction takes place much more easily than in the transverse direction. Furthermore, it has been proved that much larger quantities of latex are obtained from transverse cuts than from longitudinal cuts of the same length, and that the flow of latex is preponderantly in the vertical direction. Since latex cannot be collected from a horizontal cut (*see* subsequent discussion), it is the practice when tapping to make cuts at more or less of an angle from the horizontal. This angle amounts to about 35° in the case of *Hevea* trees. It is to be borne in mind that, with *Hevea*, as was proved by T. Petch,[39] the vessels do not run in a vertical direction, but rather in the direction of a spiral ascending toward the right. From this it follows that more vessels will be opened by making an inclined cut which rises to the left than by making one which rises to the right, at the same angle with the horizontal.

Figure 20 brings out this point diagrammatically. The light lines of this figure indicate the direction of the vessels; the heavy lines the directions of the tapping cuts. It is obvious that the rational method of tapping is shown by Diagram II of Figure 20. The difference in yields obtained with these two methods of tapping was found by E. Bateson[40] to be 14 per cent, and by A. W. K. de Jong,[41] in various experiments, 14.3 and 11.2 per cent.

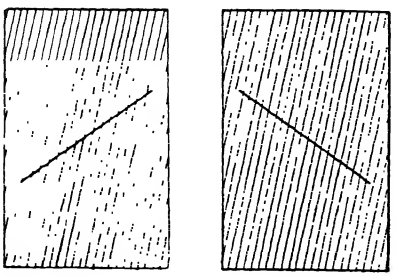


Figure 20—Diagram showing different kinds of tapping cuts and the direction of the latex vessels in the trunk of a Hevea tree.

[36] *Rubber Res. Scheme Bull.*, **75** (1918).
Arch. Rubbercultuur, **2**, 837 (1918).
[37] Bobilioff, W., "Anatomy of Hevea Brasiliensis," p. 64, Zürich, **1923.**
[39] Petch, T., "The Physiology and Diseases of Hevea Brasiliensis," p. 112, Dulan & Co., Ltd., London, **1911.**
[40] *Tropenpflanzer*, **19**, 628 (1916).
[41] *Arch. Rubbercultuur*, **3**, 1 (1919).

Upon investigating the bark of a large number of *Hevea* trees, it has been found that for trees of the same age the number of rings is the same, while for trees having bark of the same thickness the number may be quite different. This observation led to speculation regarding the existence of a relation between the number of rings and the yield of latex. That such a relation exists has been proved by various investigators.[42] In fact, the method of counting rings with the aid of a good magnifying glass has been used considerably (during experiments in plant selection, for example) in differentiating between trees of high and low yield-capacity. Such a method of determination cannot be trusted beyond a certain point, since the number of rings is not the only factor influencing the yield of latex.

H. Ashplant[43] has recently demonstrated that the distance between the individual rings can also exert an influence on the quantity of latex obtainable upon tapping. Since the tapping cut is always restricted in depth, so as to avoid danger of injury to the cambium, and since the distance between the deepest part of the cut and the cambium is always about the same (approximately 1.5 mm.), it follows that (for barks having the same number of rings) the greater the number of rings in this protected zone, the smaller should be the yield of latex. By means of this observation, Ashplant has been able partly to explain the fact that the yield of latex is greater at the base of the trunk. Since the rings are farther apart at the base, their number in the protected zone at the base is less than farther up the tree.

Ashplant[44] has also called attention to another anatomical factor which influences the yield of latex; namely, the size of the latex vessels (or "tubes," according to Ashplant's terminology). Among different *Hevea* trees the variation in "tube" bore may be considerable (21 to 51 μ). On the other hand, the variation in "tube" bore in different parts of any given tree is relatively small. A further observation of Ashplant was that a direct proportionality exists between the diameter of the latex "tubes" and the diameter of the bark cells. This observation is of practical importance, since the size of the bark cells can be measured much more easily than that of the latex "tubes." Since the wider "tubes" contain more latex and offer less resistance to its flow than the narrower ones, a larger yield from the former should be anticipated. The experiments of Ashplant have confirmed this supposition. To what extent such determinations may be used in practice as criteria for judging the yield-capacity of trees remains to be determined with exactness.

Latex

General Botanical Characteristics

That a living protoplast is still present in the completely developed laticiferous elements follows from the fact that it has been found to be possible to demonstrate in them numerous normally formed cell nuclei.[45] M. C. Potter[46] was able further to demonstrate that the starch grains observed in the laticiferous ducts of certain Euphorbiaceae are formed on leucoplasts. According to the observations of F. Kallen,[47] and H. Molisch,[48] it seems very

[42] G. S. Whitby, *Ann. Botany*, **33**, 313 (1919); W. Bobilioff, *Arch. Rubbercultuur*, **4**, 383 (1920); C. D. La Rue, *Ibid.*, **5**, 574 (1921); C. H. Gadd and G. Bryce, *Dept. Agr. Ceylon Bull.*, **68** (1924); R. A. Taylor, *Rubber Res. Scheme Bull.*, No. **43** (1926).

[43] *Bull. Rubber Growers' Assoc.*, **9**, 571 (1927).

[44] *Bull. Rubber Growers' Assoc.*, **9**, 571 (1927) and **10**, 484 (1928).

[45] See Molisch, H., "Studien über den Milchsaft und Schleimsaft der Pflanzen," G. Fischer, Jena, **1901**.

[46] *J. Linnean Soc.*, **20**, 446 (1884).

[47] *Flora*, **71**, 86 to 104 (1882).

[48] *Loc. cit.*

probable that there is in the laticiferous elements, as in all older living plant cells, a differentiation into cytoplasm and cell sap. As a result of his observations, G. Berthold[49] considered the latex to be nothing other than a metamorphosed protoplast in which, at the height of its development, there is no sap vacuole. H. Molisch showed, however, that the observations of Berthold cannot be considered evidence for such a view. How the various constituents of the contents of the laticiferous ducts are distributed in cytoplasm and cell sap cannot be stated from the available investigations. That the latex that escapes from the laticiferous ducts as a result of injury comprises a mixture of cell sap and cytoplasm follows from the fact that it was possible to demonstrate cell nuclei, leucoplasts, and starch grains in it. It cannot yet be decided with certainty, however, whether the rubber inside of the uninjured laticiferous elements is only in the cytoplasm, or in the cell sap, or in both. The first possibility is certainly rendered very improbable by the large amount of rubber contained in some latices. H. Molisch observed in longitudinal sections through fresh petioles of *Ficus elastica* a thin plasma tube, in the cavity of which the rubber particles were found. Similar observations were made also by W. Bobilioff.[50] In any case the possibility that the rubber is formed within the protoplast and from there gradually finds its way more and more into the cell sap does not seem to be excluded.*

The rubber inside the latex elements is in the form of particles, which are often approximately spherical in shape. Since a shape deviating considerably from the spherical is not infrequent, the writer prefers the term "rubber particle" to such designations as "rubber sphere" or "rubber globule." Although the particles may possess a diameter as great as several microns, many of them are too small to be perceptible in the ordinary microscope.

The liquid surrounding the rubber particles is generally designated as the "serum." The composition of the serum is quite complicated, and may vary considerably from one species to another. Colloidal material is usually present.

In the section which follows, a discussion is given of the observations which have been made in connection with the individual characteristics of the rubber particles of the various species of plants. In order to avoid repetition, the description of the non-rubber constituents present and of the chemical properties of the latex is omitted at this point and is presented in the section devoted to the chemistry of rubber. On the other hand, the physical properties of latex, and the physiological investigations which have been conducted in connection with them, are treated below, after the discussion of the individual characteristics of the particles.

The Individual Characteristics of the Rubber Particles in Various Plants

Since the rubber particles of the typical rubber plant consist chiefly of rubber itself, it is to be anticipated that they should agglomerate upon the coagulation of the latex. Whether other somewhat resin-like sub-

[49] Berthold, G., "Studien über Protoplasmamechanik," Leipzig, **1886.**

[50] *Arch. Rubbercultuur,* **9,** 313 (1925).

* Translator's Note. In a recent lecture, C. E. T. Mann, botanist of the Rubber Research Institute of Malaya, stated that the evidence now points to the fact that the protoplasmic lining of the latex vessel is the actual seat of the formation of rubber. If this lining layer is damaged (as in the early stages of brown bast), the synthesis of rubber ceases. See *India Rubber J.,* **84,** 653 (1932). V.N.M.

stances are also present in the particles (as assumed by H. Loewin)[51] has not yet been determined with certainty. This problem could probably best be settled by investigating resin-rich latices, the morphological organization of which has apparently not yet been studied. The difficulties in connection with experiments along this line are increased by the fact that the compounds concerned cannot be distinguished with certainty by means of usable microchemical methods (as proven by H. Molisch[52] and others). It is rather easy to stain the contents of the laticiferous elements by means of a solution of alkannin in equal parts of glycerol, alcohol, and water. Unfortunately this dye stains not only the rubber but also the resins and fatty oils. The method recommended for the microchemical detection of rubber in cut sections by H. M. Hall and T. H. Goodspeed [53] consists of putting the sections in 95 per cent alcohol for 5 minutes, then in boiling acetone for 15 to 30 minutes, and finally in a Sudan III-glycerol solution for 18 hours. They are then washed as quickly as possible with 50 per cent alcohol and are finally mounted in pure glycerol. This method could probably also find application in the investigation of thin films obtained by drying or coagulating latex.

The method of E. A. Hauser[54] for making the rubber particles visible is also worthy of mention. The agent used by Hauser for this purpose is Opal Blue, an aniline dye dissolved in a gelatinizing liquid. After the latex has been treated with the diluted and filtered dye solution, a slide is prepared and dried in the air. The rubber particles appear white in a blue background. As a consequence of the gelatinous consistency of the dye solution, complete drying is not possible, and a permanent preparation is obtained.

Hevea

The number of rubber particles in latex was determined by V. Henri.[55] In a sample of Hevea latex, diluted to a rubber content of 8.7 per cent, he found 50,000,000 particles per cubic centimeter. For normal 35 per cent latex this would correspond to 200,000,000 particles per cubic centimeter.

That the shape of the rubber particles may deviate from the spherical in the case of *Hevea* was probably first observed by J. H. Hart.[56] He described the shape as being oval with one end somewhat pointed.

In latex obtained from young shoots on a 32-year old tree, T. Petch[57] found some particles with a diameter of 1 μ and a large number having too small a size to be measured. In the latex from the bark along the trunk of the same tree he found particles with diameters from 0.5 to 3 μ. Many of them were provided with "tails," which were, in the cases of particles 3 μ in diameter, as great as 5 μ in length and 0.5 μ in width. From the inner bark of a tree which was similar in age but which had not been tapped before, he obtained latex with many particles of small size. "Tails" were common with these particles.

[51] *Kautschuk*, **2**, 91 (1926).

[52] Molisch, H., "Studien über den Milchsaft und Schleimsaft der Pflanzen," p. 52, G. Fischer, **1901.**

[53] *Univ. of California, Publ. in Botany*, **7**, 214 (1919).

[54] Hauser, E. A., "Latex," p. 59, Th. Steinkopff, Dresden and Leipzig, **1927.**

[55] *Compt. rend.*, **144**, 432 (1907); *Caoutchouc & gutta-percha*, **3**, 511 (1906).

[56] *Rev. cult. coloniales*, **8**, 85 (1901).

[57] Petch, T., "The Physiology and Diseases of Hevea Brasiliensis," p. 18, Dulan & Co., London, **1911.**

P. Schidrowitz[58] discovered that the size of the particles varies with the age of the plant. He observed that particles with a diameter of 1 to 2 μ might be as frequent in old trees as those of 0.5 μ in young plants. According to W. Bobilioff,[59] only round rubber particles with a diameter usually less than 0.5 μ are to be found in the latex vessels of young plants and in the young organs of older trees. On the other hand, he differentiated between four more or less overlapping types, which are to be found in the trunk of the tree; namely, (1) very small spheres having diameters less than 0.5 μ, (2) spheres with diameters between 1 and 2 μ, (3) oval or pear-shaped particles, 1.5 to 2 μ in diameter, and (4) pear-shaped particles, with diameters from 1.5 to 3 μ and tails up to 5 μ in length.

These types are to be found in quite different proportions in various trees. Upon occasion one or the other of the three types mentioned last may be missing entirely. On the other hand, the size and shape of the particles in the different parts of the trunk of any given tree are approximately constant. They are to be regarded as individual characteristics of the tree. The characteristic size and shape persist in latex which has been removed during the tapping operation, and thus form the basis of a system of differentiating between high- and low-yielding trees.

After strips of bark had been entirely isolated from the remainder of the bark by means of cuts penetrating completely to the cambium, Bobilioff observed a diminution in the size of the rubber particles upon continued tapping. The oval-shaped particles and those with tails often disappeared completely. After a long rest period, particles having the previous size and shape again appeared.

The observations of Bobilioff were essentially confirmed by H. Freundlich and E. A. Hauser,[60] and by Hauser[61] alone. However, these investigators found egg- and pear-shaped particles to predominate in very young trees, whereas the occurrence of those with distinctly tail-like appendages is limited to the older trees. By means of the "twinkling" phenomenon they proved that the ultramicroscopically small particles also possess a shape deviating from the spherical. (*See* Fig. 21.)

Figure 21—Rubber particles (*Hevea brasiliensis*).

In trees which were tapped again after a long rest period, Hauser found a high proportion of large rubber particles. For several days the average size decreased until a minimum was reached after tapping for about eight days. Upon further tapping there was an increase again for about eight days, after which time a uniform particle size was maintained.

[58] *Kolloid-Z.*, **4**, 87 (1909).
[59] *Arch. Rubbercultuur*, **3**, 379 (1919).
[60] *Kolloid-Z.*, **36**, (Supplementary Volume), 17 (1925).
[61] Hauser, E. A., "Latex," p. 57, 59, Th. Steinkopff, Dresden and Leipzig, **1927**; Kautschuk, **3**, 357 (1927).

That there exist certain particles of characteristic shape in the latex of every tree is another interesting observation made by Hauser. This individuality in shape permits the origin of a sample of latex to be determined, provided the characteristic particle shapes of all of the trees concerned have previously been observed. On the other hand, a characteristic difference was not observed between trees with rich and poor flows of latex, between healthy and sick trees, or between those at rest and those being tapped.

More recently Hauser[62] has observed that plants obtained by bud grafting usually contain particles which exhibit the characteristic shape of the mother tree. In certain cases, a shape other than that characteristic of the mother tree predominates. Whether this latter fact is to be attributed to the influence of the base stock on the particle shape or to a change in the rubber particles of the bud which was grafted on, is yet to be determined. In the case of sexual propagation the characteristic shapes of both parents are to be observed in the latex of the resulting plant. One individual form is usually predominant, however.

It should be mentioned finally that, according to Hauser, latices may be divided into two distinct classes. In one, the size of the particles deviates but slightly (from 0.5 to 1.5 μ, for example); whereas with the other, the variation in diameter may be from 0.5 to 4 μ. Trees containing the first-mentioned type of latex have smooth bark. On the other hand, trees having the second type possess a ribbed bark and often show evidences of disease.

No thoroughly satisfactory explanation of the shapes of the latex particles, and especially of the tails attached to some of them, is apparent. Such shapes have so far not been observed with artificially prepared colloid particles. That the tails could have resulted from the fusion of a larger particle with smaller ones seems highly improbable, especially in the cases of narrow extended tails.* Such cases also militate against the assumption that the shapes resulted from division of particles by a process resembling sprouting. It was at one time assumed that a deformation of the rubber particles is brought about by molecular motion. In this connection it has been pointed out[63] that the particles with tails exhibit a pronounced longitudinal vibration which is strongest at the narrower end. The demonstrated constancy of the characteristic shape makes it appear probable that the form of the latex particles is to be traced back to complicated processes, which are greatly influenced by the constitution of the protoplasm.

Differing opinions regarding the consistency and structure of the individual rubber particles in Hevea latex have already been expressed.[64] That of C. Beadle and H. P. Stevens[65] is especially noteworthy in this connection. These investigators assume that rubber particles, like drops of thick oil, unite with one another. At the moment of their fusion,

[62] *Kautschuk*, **3**, 357 (1927).

* Translator's Note. The investigations of von Weimarn [*Bull. Chem. Soc. Japan*, **3**, 157 (1928)] are of interest in this connection. He considers latex to be a polydisperse system of iso-aggregated particles (iso-spherulites), the general consistency of which is fluid-gelatinous. He was also led to believe that the serum constituents are present not only on the surface film but also on the inside of the latex particle and play an important role in the changes the iso-aggregates undergo during the drying and other coagulating processes. Moreover, he has reported that in certain cases some of the particles flow together. Especially was this true when the temperature was raised to 100° C., or when the protein film was removed with a "dispergator," such as lithium iodide. V.N.M.

[63] Anon., *India Rubber World*, **68**, 703 (1923).

[64] See Hauser, E. A., "Latex," p. 65, Th. Steinkopff, Dresden and Leipzig, **1927**.

[65] *Kolloid-Z.*, **13**, 207 (1913).

bodies with the shape of dumb-bells, eggs or pears are formed. These gradually assume a spherical shape.

The experiments of Freundlich and Hauser[66] have cast considerable light on the structure of the latex particles. Use was made of the ultramicroscope, the micromanipulator, and of photographic and cinematographic methods, during the studies made by these investigators. They found the rubber particle to possess a thin outside layer or shell of tough elastic material. The striking elasticity and the insolubility of the shell in water and other solvents prove that it cannot consist of proteins. It was also observed that the rubber particle swells considerably in benzene, the diameter increasing to three or more times its original value. Upon bursting the shell, they observed that the inner contents behaved as a homogeneous fluid mass. When the swollen particle was punctured with a micromanipulator needle the liquid inside flowed out immediately, while the outside skin remained on the needle. It therefore appears that the shell must be insoluble in benzene, but so permeable to the latter that swelling of the inner contents can take place.

A further assumption of Freundlich and Hauser is that the Hevea rubber particle is also surrounded by a layer of adsorbed material. This layer consists chiefly of proteins, but may also contain certain resins. They reached this conclusion upon observing: (1) that latex gives an irregular series with hydrogen ions, (2) that proteins, removed from the latex by filtration, coagulate at the same pH value as does the latex, and (3) that, when the proteins of the fresh latex are digested with trypsin, the rubber particles fuse together more easily upon coagulation than is the case with normal latex.

Mrs. N. Beumée-Nieuwland* [*Arch. Rubbercultuur,* **13,** 555 (1929)] disagrees with the assumption made by Freundlich and Hauser as to the constitution of the layer of adsorbed material on the surface of the rubber particle. It is her opinion that latex consists of rubber globules, surrounded by a layer of lipoids (sterols, lecithin, esters of sterols) and suspended in a protein emulsion.

Freundlich and Hauser also consider that they have established the fact that the rubber hydrocarbon is in a different form when in latex than when in crude rubber. During investigations made with the micromanipulator, they could observe no change in the consistency and structure of the rubber particles in latex as long as an aqueous dispersion medium remained present. As soon as all of the water was evaporated, the particles could no longer be separated from one another upon the addition of water. The inner fluid material of the particles became more and more viscous until it finally all went over into the gel form. The contours of the particles remained the same, the outside shells thus functioning as a framework to a certain extent. The shells also became considerably more solid in consistency.

Whether, in the case of *Hevea,* all rubber particles have the same constitution is a question which cannot be answered definitely. O. de Vries[67] considers it possible that the rubber particles from young trees and from leaves possess a composition or a degree of polymerization differing from those of the particles from the bark of old trees. The fact that rubber from the former vulcanizes to give a softer product provides some experimental evidence in favor of this assumption. The higher

[66] *Kolloid-Z.,* **36,** (Supplementary volume), 24 (1925).

* Translator's note by H. W. G.

[67] de Vries, O., "Estate Rubber," p. 12.

resin content of the latex from young trees may also exert some influence on these results, however.

Manihot

It was J. H. Hart[68] who first expressed the opinion that in the case of *Manihot Glaziovii,* the rubber occurs in the form of small elongated rods. The writer[69] has also observed in fresh latex of this type minute spheres and larger grainy bodies which are generally spherical in shape (Fig. 22).

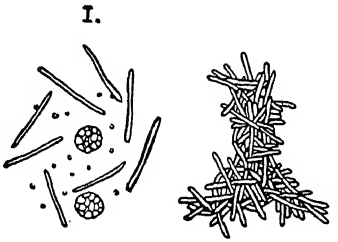


Figure 22—*Manihot Glaziovii.*

I. Various particles present in the latex.
II. Rubber particles agglomerated by coagulation.

Since the little rods, which are less than 1 μ in width and may be 10 μ or more in length, constitute the predominant material in the latex from the older bark, and since this latex agglomerates to a compact network upon being coagulated, it cannot be doubted that the rods consist of rubber. On the other hand, the composition of the small spheres remains undetermined. Since F. Tobler[70] has proved that rubber is always present in the latex of young trees, although rods may be entirely missing, it seems highly probable that the tiny spheres correspond to the rubber particles of other rubber plants. The larger granular spheres are colored yellow or brown by a solution of iodine. The writer has expressed the view that they possibly represent deformed nuclei. However, after it was demonstrated by Tobler[71] that these particles are contained only in the first few drops of latex flowing from a wound, it appeared possible that they do not originate in the latex vessels at all, but in some other part of the bark, such as the sieve-tubes. In explaining the deficiency of rubber rods in the latex collected from young trees, Tobler has assumed that upon the beginning of coagulation the rods are retained in the ends of the latex vessels more readily than are the rubber spheres. The investigations of Tobler do not disclose the conditions which must exist before the rubber rods are released.

According to Freundlich and Hauser,[72] who did not concern themselves with the spheres, the rubber rods consist of extremely tough, tacky, homogeneous material. By suitable manipulation the rods can easily be made to unite to form masses lacking in uniformity. There is no evidence of any adsorption layer around the rods. Freundlich and Hauser assume furthermore that, upon coagulation or evaporation, the individual particles come together without definite orientation. As they come into closer contact, they fuse into a homogeneous mass which gradually solidifies and takes on the characteristics of crude rubber.

[68] *Rev. cult. coloniales,* **8,** 81 (1901).
[69] See Zimmermann, A., "Der Manihot-Kautschuk," p. 133, G. Fischer, **1913.**
[70] *Jahrb. wiss. Botan.,* **54,** 293 (1913).
[71] *Ibid.,* **54,** 291 (1913).
[72] *Kolloid-Z.,* **36** (Supplementary volume), 29 (1925).

Castilloa

According to J. H. Hart,[73] the rubber particles in *Castilloa* latex vary greatly in size. E. Fickendey [74] mentions 2 to 3 μ as the diameter of the particles.

According to C. O. Weber,[75] the rubber particles are surrounded by a shell having usually a smaller optical refractive power than the rubber itself. The behavior of this shell towards an iodine solution indicates that it consists of proteins. From its insolubility in alcohol, the conclusion is drawn that it is not composed of resinous compounds. Freundlich and Hauser [76] also concluded, from their investigations, that the Castilloa rubber particles are surrounded by a layer which protects them to such an extent that no flattening is to be observed when individual particles come together.

Upon observing under the microscope that pressure on the cover glass resulted in bursting the large rubber particles and allowing their contents to flow out, Weber concluded that the particles possess a liquid consistency. C. Beadle and H. P. Stevens[77] observed, moreover, that fusion takes place upon pressing the particles together. Freundlich and Hauser also concurred in the belief that the particles have a fluid consistency.

The investigations of R. Ditmar,[78] A. W. K. de Jong and W. R. Tromp de Haas,[79] C. Harries,[80] and W. Esch and A. Chwolles[81] cast considerable doubt on Weber's assumption that polymerization of the rubber occurs when it goes over from the liquid to the solid state of aggregation.

Ficus

The diameters of the rubber particles in the latex of *Ficus elastica* vary from 2 to 3 μ, according to E. Fickendey.[82] Freundlich and Hauser [83] measured some with diameters of .5 μ, however. (Fig. 23.) Beadle and

I II III

Figure 23—Rubber particles of *Ficus elastica*.

I. From fresh latex.

II and III. During and after the evaporation of the coagulating agent. (Courtesy of E. A. Hauser.)

Stevens[84] reported that upon standing the small rubber particles gradually disappear by uniting into agglomerates of various sizes. The particles have more the appearance of an oily liquid than of solid bodies. Freundlich and Hauser stated that the particles are entirely liquid and are not surrounded by a solid shell. The presence of a thin adsorption layer, probably consisting of resins, can be recognized on the larger particles by using the ultramicroscope.

[73] *Rev. cult. coloniales*, **8**, 85 (1901).
[74] *Tropenpflanzer*, **13**, 205 (1909).
[75] *Gummi-Ztg.*, **19**, 101 (1904).
[76] *Kolloid-Z.*, **36** (Supplementary volume), 29 (1925).
[77] *Kolloid-Z.*, **13**, 214 (1913).
[78] *Chem.-Ztg.*, **29**, 175 (1905).
[79] *Ber.*, **37**, 3301 (1904).
[80] *Gummi-Ztg.*, **24**, 850 (1910).
[81] *Ibid.*, **19**, 165 (1904).
[82] *Tropenpflanzer*, **13**, 205 (1909).
[83] *Kolloid-Z.*, **36** (Supplementary volume), 28 (1925).
[84] *Ibid.*, **13**, 209 (1913).

Kickxia

The rubber particles of *Kickxia elastica* possess diameters of only 0.5 μ (or sometimes less), according to E. Fickendey.[85] Hauser[86] states that the latex contains particles for the most part of ultramicroscopic size. Those visible in the light field exhibit a marked pear shape with short appendages. Fickendey[87] noticed that the individual particles flow together upon coagulation of the latex. He observed, moreover, that the particles seldom unite to form spherical aggregates, but generally remain as extended agglomerates, often with a constriction in the middle.

Mascarenhasia

In the case of *Mascarenhasia elastica*, wounds in the leaves or stems of young trees may lead to the flow either of a clear juice or of a very milky liquid. In fact, both may flow simultaneously from different parts of the same tree. On the other hand, normal latex is always obtained from the bark of older trees upon tapping. The colorless juice contains protein and rubber-like substances, according to F. Tobler.[88] He also found present "shining grains" ("glänzende oder spanförmige Körner"), which were up to 15 μ in length and 5 μ in width, and which could be colored red with alkannin. Whether these consist of rubber, as Tobler assumed, is still to be proved. No exact investigations of the composition of the normal latex appear to have been made.

Physical Properties of Latex

Colloidal Character. Fresh latex is a complex system in which serum forms the dispersing medium and rubber particles the dispersed phase. The serum is not, however, a simple solution, as proteins may be colloidally dissolved in it.

There has been much dispute concerning the group of colloidal systems to which latex shall be assigned. It was placed in the emulsoid class by A. T. Borrowman[89] and in the suspensoid by F. Kirchhof.[90] According to microscopic investigations made on the rubber particle, many of which show the particle to possess a liquid and others at least a very viscous consistency (*see* p. 55 and following), the assumption that latex should receive a place between the emulsoid and suspensoid classes appears correct.

Latex was placed first in the hydrophilic or lyophilic, and then in the hydrophobic or lyophobic class. When it is considered that the coagulum obtained from latex is very rich in water and corresponds to a gel resulting from a hydrophilic sol it may seem correct to assign latex to the hydrophilic class. Since, in coagulation, the surrounding adsorption layer and not the rubber particles themselves often play the leading role, and since the rubber particles are able to take up or hold only a small amount of water, it is more correct to designate latex (as does P. Scholz[91]) as a hydrophobic sol protected by protein.

[85] *Tropenpflanzer*, **13**, 205 (1909).
[86] Hauser, E. A., "Latex," p. 88, Th. Steinkopff, Dresden and Leipzig, **1927.**
[87] *Kolloid-Z.*, **8**, 46 (1911).
[88] *Jahrb. wiss. Botan.*, **54**, 275 (1914).
[89] "Rubber Industry," (ed. by J. Torrey and A. S. Manders), The International and Allied Trades Exhibition, Ltd., London, p. 243, **1911**
[90] *Kolloid-Z.*, **35**, 367 (1924).
[91] *Kautschuk*, **4**, 5 (1928).

The rubber particles in fresh latex exhibit a very energetic Brownian motion, which, as will be thoroughly discussed in the section on coagulation, can be stopped by different reagents.

As was first proved by V. Henri,[92] with preserved and dialyzed *Hevea* latex, the rubber particles migrate to the positive pole upon passage of an electrical current through the latex. They are, therefore, negatively charged. The same is also true for the rubber particles of *Kickxia,* according to D. Spence[93] and P. Schidrowitz.[94]

Surface Activity. According to the investigations of E. A. Hauser and P. Scholz,[95] *Hevea* latex contains a very strongly surface-active material which lowers the surface tension of the solvent almost as much as ordinary soap. The value for surface tension decreases with increasing dilution until a minimum is reached at 1/64 of the original concentration. Then it rises again, but even at a concentration of 0.05 per cent a noticeable effect is to be observed. In latex preserved with ammonia, a lowering of the surface tension and accordingly an increase of the surface activity was found to have occurred. A surface-active substance was to be detected in the serum remaining after the coagulation.

Specific gravity. The specific gravity of latex is diminished by the rubber particles contained in it but increased by the dissolved material. According to O. de Vries,[96] the average specific gravity of the rubber particle is 0.914 and that of the serum is 1.020. The specific gravity of fresh *Hevea* latex usually varies between 0.978 and 0.987. It can amount to about 1 only in latex with a very small rubber content. In latex having a rubber content of but 16 per cent (obtained from a tree which had been strongly tapped), de Vries found the specific gravity to be 1.0002. On the other hand, P. van Romburgh [97] found a specific gravity of 0.966 for latex which contained 48 per cent of rubber, and G. Vernet [98] stated that some latices have a specific gravity of only 0.9555.

According to A. Moulay,[99] the latex of *Manihot Glaziovii* has a specific gravity of 1.02 to 1.03. P. van Romburgh [100] states that its specific gravity is 1.021 at 27° C. With *Ficus elastica,* the specific gravity of the fresh latex varies between 0.957 and 0.985, and is lowest in rubber-rich latex, according to P. van Romburgh. The same author observed values lying between 0.994 and 1.009 in the case of *Castilloa.* The specific gravity of *Kickxia* latex was stated by E. Fickendey [101] to be from 0.979 to 0.988 and by D. Spence[102] to be 0.990. The latices of *Euphorbia Cyparissias* and *E. platyphylla,* which contain little rubber, were found by A. Weiss and J. Wiesner[103] to have specific gravities varying from 1.0449 to 1.0468.

In practice, specific gravity determinations are very frequently used for rapid and sufficiently accurate estimations of the rubber content of latices (*see* p. 110). Various instruments (latexometer and metrolac, among others) are used for this purpose. Their use and the resulting sources of error were described by O. de Vries[104] and E. A. Hauser.[105]

[92] *See* "Lectures on India Rubber," edited by D. Spence, p. 203, **1909.**
[93] *Kolloid-Z.,* **4,** 204 (1909).
[94] Schidrowitz, P., "Rubber," p. 116, Methuen & Co., London, **1911.**
[95] *Kautschuk,* **3,** 332 (1927).
[96] de Vries, O., "Estate Rubber," p. 39.
[97] *Mededeel. uit's Lands Plantentuin,* **39,** 94 (1900).
[98] Lucien Morisse, "Le latex; son utilisation directe dans l'industrie" p. 566, H. Challamel, Paris, **1908.**
[99] *L'agr. prat.,* **5,** 368 (1905).
[100] *Mededeel. uit's Lands Plantentuin,* **39,** 102 (1900).
[101] *Tropenpflanzer,* **13,** 203 (1909).
[102] *Chem. Zentr.,* **79,** *I,* 842 (1908).
[103] *Botan. Ztg.,* **19,** 41 (1861) and **20,** 124 (1862).
[104] *Arch. Rubbercultuur,* **3,** 183 (1919) and "Estate Rubber," p. 113.
[105] "Latex," p. 75, Th. Steinkopff, Dresden and Leipzig, **1927.**

Viscosity. The viscosity of freshly obtained latex has been investigated repeatedly. It was shown by O. de Vries[106] that, as a consequence of the formation of flocs and the occurrence of decompositions, these determinations are affected by errors of observation to a greater extent than is the estimation of the viscosity of benzene solutions of rubber.

This also holds true for ammonia-preserved latex, although more reliable results are obtained with it than with fresh latex or latex diluted with water.

Physiology of Latex

Origin of the Rubber. It is very probable that rubber is formed in the laticiferous elements, since it has not as yet been possible to detect it in other cells, especially in the parenchyma cells surrounding the laticiferous elements. Furthermore, since a living protoplast is present in the laticiferous element, even after the complete development of the latter, the possibility exists that the rubber-forming processes take place in the protoplast. In which organ of the plant the rubber is formed is a question still to be answered. A view which has been expressed repeatedly is that the formation of rubber stands in direct relation to the rate of assimilation by the green cells, and that the rubber is formed exclusively in the leaves, from which it moves to the non-assimilating (non-photosynthetic) parts, especially to the trunk and the roots. If this view is correct a very energetic movement of material must take place (especially in large trees), since diffusion and osmosis cannot come into question as the moving forces. Protoplasmic streaming, according to the few observations which have been made on the motion taking place in the latex vessels, is also not sufficient to explain such a rapid transportation of material.

It was shown by R. H. Lock[107] that the latex contained in the trunk is usually richer in rubber than that occurring in the leaves. W. Bobilioff[108] found also that a new formation of rubber can take place in a strip of bark which is completely isolated from the bark of the upper trunk by a channel cut through to the cambium. Finally it was determined[109] that the formation of latex likewise takes place in stumps and beneath the rings of ringed trees. Therefore it must be regarded as proved that rubber can be formed even in non-photosynthetic organs. At least it is very probable that rubber is naturally formed where new laticiferous elements are found, provided the necessary raw materials are present in sufficient amounts. Various authors have even connected the formation of rubber with the disappearance of carbohydrate contained in the storage tissues of the wood and bark. However, this disappearance is probably occasioned primarily by the effect of the tapping wound in interrupting the conducting channels in the bark and by the necessity for restoring the cortical tissues on the tapped surface. That rubber is formed directly from the carbohydrate, as was assumed by C. Harries,[110] cannot yet be regarded as certain. In any case, it does not appear impossible that the rubber in the living plant is formed as a compound of complex structure and is a decomposition product of the

[106] *Arch. Rubbercultuur*, **23**, 409 (1923).
[107] Lock, R. H., "Rubber and Rubber Planting," p. 69, Cambridge, **1913**.
[108] *Arch. Rubbercultuur*, **3**, 392 (1919).
[109] *Arch. Rubbercultuur*, **2**, 289 (1918) and 4, 227 (1920).
[110] *Ber.*, **48**, 1198 (1915).

metabolism. In this connection, D. Spence[111] expressed the opinion that perhaps the resinous compounds occurring in the latex represent a by-product of or an intermediate stage in the decomposition of the rubber in the plant. As far as the present author knows, no proof of this assumption has appeared.

Function of the Latex. Various authors have ascribed to the latex vessels and tubes the function of substituting for or assisting the sieve-tubes and the conducting parenchyma in the transportation of the plastic foodstuff of the plant, especially the proteins and carbohydrates. However, it was reported by H. Kniep[112] that the results of previous investigations do not particularly support the assumption that the laticiferous ducts play any important part in the transportation of foodstuffs.

That the laticiferous elements serve as reserve storerooms for proteins, carbohydrates, or fats is another view which has often been expressed. According to the investigations of M. Treub,[113] S. Schullerus,[114] and C. Bernard,[115] it can be regarded as a known fact that the starch granules occurring in the latices of many species of *Euphorbia* are dissolved when assimilation is inhibited for a long time. An appreciable decrease of the latex starch did not take place in various cases until the starch in the surrounding parenchyma had already been completely dissolved, according to H. Kniep.[116] The investigations of D. Bruschi[117] and F. Tobler,[118] from which it was concluded that the fats, proteins, and other constituents of the latex are consumed within the plant, may be given another interpretation. It appears doubtful whether such materials are ever consumed in considerable quantity during the normal development of the plant. They are perhaps used only in the metabolism of the laticiferous elements or serve for the nutrition of other tissues.[119] A. Onken[120] sought to prove that the laticiferous elements of many plants serve as storehouses in which the lime separated during metabolism is made harmless. Such a function could be possible only in a limited number of species.

At the present time it cannot yet be regarded as proved that the rubber contained in the laticiferous elements again finds use in the metabolism of the plant. After C. Harries had come to the conclusion that the rubber hydrocarbon stands in close relation to the carbohydrate, the view that carbohydrates can again be regenerated from rubber in the living plant was offered by R. Ditmar[121] and D. Spence.[122] P. Schidrowitz[123] expressed the idea that perhaps the resinous bodies, especially those accompanying tackiness of the rubber, can play a role in the regeneration of the rubber to assimilable material. Exact physiological experiments, leading to results which speak for the correctness of these assumptions, do not as yet appear to have been made.

[111] "Lectures on India Rubber," p. 194, **1909.**
[112] *Flora*, **94**, 129 (1905) and "Rubber Recueil," 63.
[113] *Ann. de l'inst. bot. de Buitenzorg*, **3**, 37 (1883).
[114] *Verhandl. d. Botan. Vereins d. Provinz Brandenburg*, **24**, 26 (1882).
[115] *Ann. jard. bot. Buitenzorg (supplement)*, **3**, 235 (1910).
[116] *Flora*, **94**, 151 (1905).
[117] *Ann. di botanica*, **7**, 671 (1909).
[118] *Jahrb. wiss. Botan.*, **54**, 265 (1914).
[119] See also W. Bobilioff in *Arch. Rubbercultuur*, **2**, 293 (1918).
[120] *Bot. Archiv.*, **2**, 281 (1922).
[121] Ditmar, R., "Die Analyse des Kautschuks, der Guttapercha, der Balata und ihrer Zusätze," p. 36, Vienna, Leipzig, **1909.**
[122] "Lectures on India Rubber," edited by D. Spence, p. 199, **1909.**
[123] Schidrowitz, P., "Rubber," p. 171, Methuen & Co., London, **1911.**

According to J. Parkin,[124] W. G. Freeman,[125] P. Olsson-Seffer,[126] and E. Fickendey,[127] the laticiferous element serves as a water reservoir. However, confirmation of this assumption as a consequence of exact experiments has not been obtained. On the other hand, it was observed by W. Bobilioff[128] that the water content of latex in the fruit of the *Hevea* tree decreased only slightly upon interruption of the water supply and continuation of transpiration. On the basis of the foregoing assumption it would also be difficult to understand why such large amounts of rubber, resins, proteins, etc. are contained in many latices.

E. Stahl[129] was the first to express the view that latex serves as a protective agent against animal feeding. He assumed that as soon as a plant is bitten by a small animal the latex passes from the opening in the affected part into the mouth of the attacker and tends to discourage him from further feeding. H. Kniep [130] mentioned several experiments in which it was found that many plants are not attacked by snails as long as they contain latex. He observed that various species of *Euphorbia*, which are spared by snails under normal conditions, are eagerly consumed when the latex is exhausted by repeated tapping. He made similar observations on numerous other plants when he washed out the latex contained in leaves by repeated soaking in fresh water. It was proved by F. Tobler,[131] that many latex-containing leaves are attacked by snails in the tropics. In the case of *Mascarenhasia elastica*, however, he was able to confirm the observation of Kniep that the snails disdained the leaves containing latex but ate the ones which were free from latex.

Some observations indicating that latex can protect the plant containing it from attack by insects have also been made. Thus P. Wurth[132] found that bark beetles when placed on living *Hevea* and *Kickxia* twigs, were hindered from penetrating by the latex flow caused by the attack, and were usually stuck fast, as in a trap. It was further stated by R. H. Lock [133] that bark containing no latex (as a consequence of disease or other causes) was attacked at once by boring insects, which seldom or never tasted bark rich in latex.

The view that latex serves exclusively for wound protection, and functions primarily by hindering the penetration of bacteria and air into the tissues of the plant was first offered by H. de Vries.[134] H. Kniep[135] and others have observed, however, that various latex-bearing plants close their wounds against the atmosphere by the formation of wound-cork (just as do plants containing no latex). The latex at best may only serve to close the wound temporarily; and even for this purpose it appears to be unsuited, since protein-rich latex putrefies readily and is subject to attack by bacteria and fungi as long as it is not completely dry. It was also proved by C. Bernard[136] that when latex is left on the wound in a *Castilloa* or *Hevea* tree, the healing of the wound is slowed up and the danger of infection increased. According to Koketsu,[137] protection from infection by fungi is provided by latex in the case of wounds

[124] *Roy. Botan. Gard. Ceylon, Circ., Ser.* **1**, 114 (1899).
[125] *Gummi-Ztg.*, **22**, 1123 (1908).
[126] *Agr. Bull. Str. Federated Malay States*, 20 (1907).
[127] *Tropenpflanzer*, **14**, 481 (1910).
[128] *Arch. Rubbercultuur*, **5**, 367 (1921).
[129] Stahl, E., "Pflanzen und Schnecken," G. Fischer, Jena, **1888**.
[130] *Flora*, **94**, 185 (1905).
[131] *Ber. deut. botan. Ges.*, **31**, 617 (1913).
[132] *Cultuur gids*, 73 (1908).
[133] Lock, R. H., "Rubber and Rubber Planting," p. 52, Cambridge, **1913**.
[134] *Landw. Jahrb.*, **10**, 687 (1881).
[135] *Flora*, **94**, 183 (1906).
[136] *Ann. jard. bot. Buitenzorg (Supplement)*, **3**, 259 (1910).
[137] *Botan. Mag.*, **27**, 133 (1913).

in *Ficus erecta*. He found the wounds covered with latex to be free from fungi, whereas those not covered with latex were infected.

Methods of Separating Rubber from the Plants

There are three different methods for the separation of rubber from the plants. In the first, which will be designated as the direct method, the rubber plants or parts of rubber plants are collected, and the commercial rubber is obtained directly from them by extraction or by mechanical means. In both of the other methods, the rubber plants are wounded in some way, and the commercial rubber is manufactured from the latex which flows from them. In these latter methods a distinction is to be drawn between that involving the removal of the latex from a felled tree and that in which the latex is obtained by tapping and the productivity of the tree is not impaired. In both methods, latex can either be collected in liquid form or coagulated directly on the tree.

The Direct Method of Obtaining Rubber

The direct method is always used with those species of plants in which the rubber is inclosed within a cell from which the latex can flow only when that particular cell is cut. Of these plants only the guayule shrub (*Parthenium argentatum*), from which considerable amounts of rubber are produced in southern Mexico, is important. These shrubs, which may be up to a meter in height, contain rubber in almost all parts, but especially in the stalks and root bark. The rubber was at first isolated by extraction from the collected plants after previous drying and pulverizing. Mechanical contrivances appear to have found more use lately. According to F. E. Lloyd,[138] the plant material is first ground between rolls rotating at an uneven speed and is then further pulverized in a pebble-mill, water being added in the process. The pulp so obtained is decanted in large tanks, in which the largest part of the non-rubber residue sinks while the rubber rises. The latter is, however, contaminated with air-containing scraps of wood and similar material, and is therefore subjected under water to a pressure of about 225 pounds. It is then further purified in a beater-washer. Finally it is pressed between smooth rolls and is then ready for shipping. It was also recommended that the bagasse obtained by grinding the plant be boiled in a solution of sodium hydroxide (1 to 2 per cent) in order to facilitate the isolation of the rubber and to saponify the resins partly. The resin content of the product is thus decreased from 20 per cent to 17 or 18 per cent. In guayule production still other methods, partly secret, appear to be used.

According to D. Spence and C. E. Bone,[139] it is of advantage to the quality of the rubber if the harvested bushes are stored for a long time before further working. The storage causes certain changes to take place in the rubber. According to the statement of the previously named authors, rubber produced in this manner and extracted with acetone is comparable with Hevea rubber. It is also characterized by the ease with which compounding ingredients can be incorporated in it.

[138] Lloyd, F. E., "Guayule; A Rubber Plant of the Chihuahuan Desert," p. 9, Carnegie Institution of Washington, **1911.**

[139] *Gummi-Ztg.*, **42,** 857 (1928) and Spence, D. and Bone, C. E., *Tech. Papers, Bur. Standards* **No. 353,** (1927).

The direct method of obtaining rubber is also used with such plants as contain the rubber preponderantly in the roots or underground root stock or which have such small dimensions that tapping is not profitable. To this class belong especially the various species of Apocynaceae which yield the so-called root or herb rubber. They are found particularly abundantly in the dry parts of Angola. According to H. Baum,[140] the first step in the method of separation used by the natives of Angola is to soak the roots (Fig. 24) in order to make the bast soft and tender (so

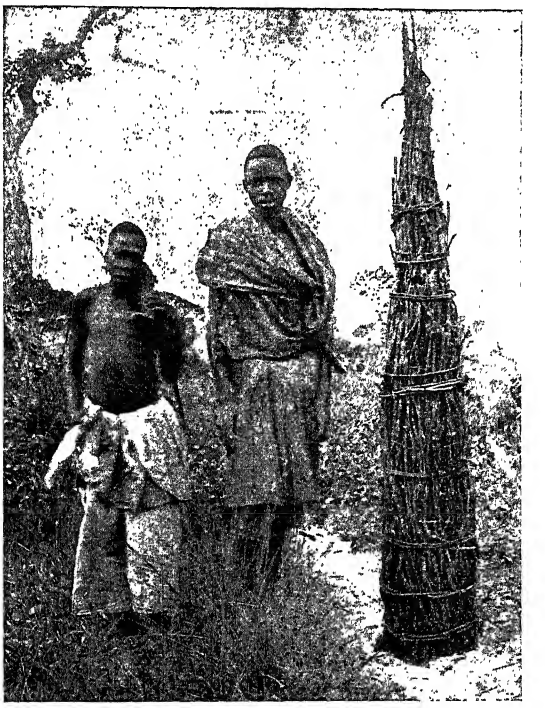


Figure 24—Rhizomes bound into a bundle.

(Courtesy of H. Baum.)

that it can be thoroughly disintegrated by later beating). The roots are then dried in the sun and cut into pieces 30 to 40 cm. long. The rubber clumps found on the ends of the roots are detached and separated from the remainder of the rubber to form a commercial grade which is mixed with considerable sand. The pieces of root are beaten on a board to remove the bark from the wood. The pieces of bark are then beaten on a board with a wooden hammer until they have assumed the form of cakes. (*See* Fig. 25.) As soon as the greatest part of the bark is removed, these cakes are boiled and then thoroughly beaten with clubs. The cakes are then cut into square pieces, placed in boiling water, and are, while still hot, formed into the round strips (of the size of the finger or thumb) which are designated in the trade as Matali.

[140] Baum, H., "Kunene-Sambesi-Expedition," p. 100, Kolonialw. Komitee, Berlin, 1903.

According to H. Jumelle,[141] rubber is obtained by the natives in a similar manner from the bark of the trunk and roots of the *Mascarenhasia lisianthiflora* in Madagascar. The process of Leembruggen[142] for obtaining rubber from the *Willughbya firma* vine in Sumatra consisted of dipping the cut stem in boiling water and isolating the rubber mechanically from the separated bark.

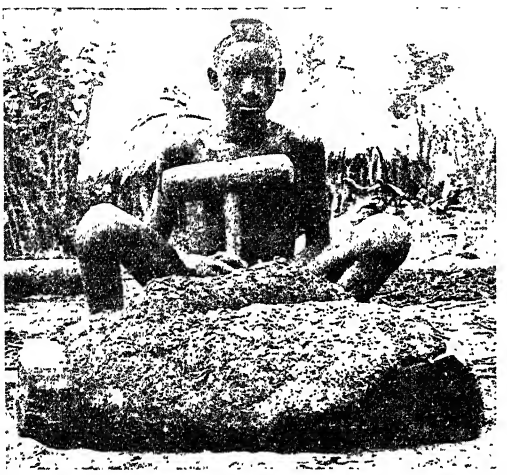


Figure 25—Production of a rubber cake by hammering.

(Courtesy of H. Baum.)

A somewhat similar method * is used in obtaining the rubber from the roots of the tau-sagyz plant, the cultivation of which is expected to provide Soviet Russia with a rubber supply of some magnitude. It is reported that the roots of this plant need merely be dried and then run through a primitive flour mill in order to separate the rubber. As an alternative method, the plant can be soaked in water and the fibers are thereby separated from the rubber. [*See U. S. Dept. Commerce, Bur. Foreign and Domestic Commerce, Special Circ.* **Nos. 3313** and **3359** (1932)].

According to E. de Wildeman and L. Gentil,[143] successful attempts have been made to replace hand work by mechanical arrangements in the production of rubber from rhizomes in the Congo region. P. Schidrowitz[144] reports that a machine constructed by Guignet is used for this purpose in Madagascar.

Repeated attempts have been made to obtain rubber from the bark, leaves or young sprouts of the trees from which rubber is usually obtained by tapping of the trunk. It has been stated that 8 per cent of good rubber could be obtained from one-year old *Castilloa* plants and that by the use of this method a profit of 2000 to 4000 marks per hectare could be obtained. According to H. G. Granger,[145] rubber has been produced in Colombia from the leaves of *Manihot Glaziovii* trees with the help of a small hand-operated mangle from Squires & Co. of Buffalo.

Although it does not appear improbable that rubber can be produced by mechanical working more profitably than by the customary process

[141] "Rubber Recueil," 38.
[142] *Teysmannia*, 353 (1899).
Translator's note by V. N. M.
[143] de Wildeman, E. and Gentil, L. "Les lianes caoutchoutifères de l'État Indépendant du Congo," p. 147, Brussels, **1904.**
[144] Schidrowitz, P. "Rubber," p. 114, Methuen & Co., London, **1911.**
[145] *India Rubber World*, **17**, 112 (1906).

through lessening of the cost due to hand work, consideration must still be given to the fact that the rubber present in the leaves and in the bark of the young branches of many species is of very low quality, even though excellent rubber is to be found in the bark of older trunks. Moreover, relatively little rubber is present in the bark of the best rubber-yielding trees (*Hevea* and *Manihot*), and it is only by the formation of new rubber, as a consequence of tapping, that these trees maintain such high yields. According to J. Parkin,[146] the latex which flows from the leaves and young shoots of *Castilloa* trees grown in Ceylon contains resins and other substances, but no, or only very little, rubber. A darker rubber of good quality has been isolated by P. van Romburgh[147] from the bark of 14-year-old *Castilloa* trees in Buitenzorg. The amount of rubber obtained, however, was only 4 per cent of the amount of dry bark. A. J. Ultee[148] obtained 2.22 to 3.03 per cent of air-dried material (low quality rubber) from pulverized leaves of *Ficus elastica*. Research conducted on *Manihot Glaziovii* gave few encouraging results.

P. Alexander and K. Bing[149] were able to extract with benzene only 1.4 per cent of the dry substance (half of which was soluble in acetone) from the bark of ¾-year old *Manihot Glaziovii* trees. The remaining half of the material was probably impure rubber.

Method of Obtaining Latex from Felled Plants

The collection of latex from felled trees is a method frequently used by the natives, since the greatest possible yield of wild rubber is thus obtained in the shortest possible time. The yield capacity of the trees is naturally more or less completely destroyed for a long time. Even when new shoots grow out of the stumps of the felled trees they are usually choked by the thick forest, and even in the most favorable cases a long time will be required before they are sufficiently grown to be tapped again.

This method of tapping is used in Brazil and adjacent countries, especially with *Castilloa*. The trees are cut down close above the earth, and then cuts extending to the wood (and usually ring-shaped on the trunk) are made, first on the boughs and then on the trunk. The latex flowing out is collected in gourds or tin cups. According to P. Preuss,[150] the trees in Peru are sometimes tapped twice in this manner by placing new rings between the first ones two to four weeks after the first tapping. By this procedure about half as much rubber may be obtained as on the first tapping. In Central America, also, *Castilloa* trees are frequently felled for the production of rubber. Certain rubber-yielding species of *Sapium* in South America are usually also cut down for this purpose. In Ecuador, according to P. Preuss,[151] they are tapped two or three weeks after felling the first time, and after a further two to three weeks are tapped the second time. R. Henriques [152] stated further that the wild rubber trees in Africa (such as the *Kickxia elastica* of Cameroons and from the vicinity of Lagos) are felled by natives to obtain the rubber, and the latex is obtained from ring-formed

[146] *Roy. Bot. Gard. Ceylon, Circ.*, **1**, 117 (1899).
[147] van Romburgh, P., "Les plantes à caoutchouc et à gutta-percha," p. 80, Batavia, **1903.**
[148] *Cultuur gids*, **1**, 893 (1910).
[149] *Tropenpflanzer*, **12**, 65 (1908).
[150] Preuss, P., "Expedition nach Central- u. Südamerika," p. 379, Berlin Kolonialw. Komitee, **1901.**
[151] *Ibid.*, p. 384.
[152] Henriques, R., "Der Kautschuk und seine Quellen," p. 19, Dresden, **1899.**

channels cut in the trunk. Rubber is obtained in a similar manner in Madagascar from *Mascarenhasia arborescens*, according to H. Jumelle,[153] and from *Ficus Supfiana*, according to R. Schlechter.[154] (*See* Fig. 26.)

Figure 26—Rubber production from *Ficus Supfiana*.
(Courtesy of R. Schlechter.)

Rubber is obtained from vines in Africa in a somewhat different manner. According to A. Chevalier,[155] the vines are cut down as close as possible to the earth and cut into pieces 15 to 20 cm. long. The latex flowing from the cuts is collected after it coagulates. The stump very quickly puts forth new vines. It is reported that in Togo the vines are left standing during the first tappings and are only felled when they give a small yield. They are then cut to pieces to obtain the remainder of the rubber.

According to the statement of H. Semler,[156] Asiatic vines are usually felled for the production of rubber. Rubber is obtained, especially from the *Willughbya firma*, by cutting the stem into pieces a few centimeters to 1 meter in length and placing the portions on a piece of wood over a large vessel in which the drops of latex are collected. When the flow almost stops, it is again stimulated by lighting a fire around the vessel.

Methods of Tapping the Rubber Plants

Of the various methods of tapping rubber trees, that which, with a similar amount of work, yields the greatest amount of good rubber over a longer period of time, and which damages the tree the least (so that the plantation will remain productive the greatest possible length of time) is in general to

[153] "Rubber Recueil," 38.
[154] Schlechter, R., "Gutta-Percha und Kautschuk Expedition," p. 133, 1911.
[155] *L'agr. prat.*, 3, 64 (1908).
[156] Die tropische Agrikultur II, Aufl. Wismar, 2, 715 (1900).

be designated as the most rational. The size of the yield naturally depends to a large degree upon the form, dimensions and direction of the tapping wounds. These factors can also be of influence upon the amount of latex which can be obtained in a liquid form and free from impurities. The desirability of a tapping method depends on how often it can be used over a long period of time (about a year) without the tapping becoming unprofitable or the quality of the resulting product becoming impaired. With regard to tapping cost, preference must generally be given to a method which with a smaller number of tappings gives a yield as large as or larger than any other. Still other circumstances are to be considered in tapping. It is necessary to determine at what age the tree yields good rubber and affords a profitable rubber production. The current price of rubber naturally plays an important role in this connection. The time of year in which the tapping takes place can also be of influence upon the size of the yield. Since various kinds of rubber plants act very differently upon being tapped, it must be understood that the same method is not used for all species. Moreover, quite different methods may be used for the same species in different countries. Before describing these methods, the physiological processes which occur upon tapping of the rubber plants and the influence these processes exert upon the vitality of the plants will be discussed in some detail. In order to make possible an understanding of the processes taking place upon the flow of latex, a survey of the forces acting in connection with these processes is to be presented. Following this, an explanation of the various tapping methods used in practice is to be given.

Physiology of Latex Flow

The flow of latex is caused on the one hand by the hydrostatic pressure prevailing in the uninjured laticiferous ducts and on the other by the pressure exerted by the surrounding tissues upon the contents of the ducts. As the author[157] proved by an accurate analysis of the pertinent factors, the hydrostatic pressure of the laticiferous ducts is greater, the greater is the osmotic concentration of the latex. This latter corresponds to a pressure of 10 to 12 atmospheres, according to the results of previously conducted experiments. Moreover, the greater the pressure is in the tracheal system, the more latex must flow out. This pressure becomes smaller or may even become negative when intensive transpiration takes place, and so it is understandable that in general less latex flows from living, transpiring plants than from those in which the absorption of water exceeds the transpiration. Moreover, the flow of latex must be aided by the bark-pressure and the weight of the water column present in the laticiferous ducts. It can also be proved that a dilution of the latex must take place upon wounding the duct and thereby disturbing the osmotic equilibrium. The dilution takes place more quickly, the greater the pressure is in the tracheal system, and more slowly, the more the transpiration exceeds the absorption.

The nature of the channel traversed also influences the productiveness of the latex flow. The narrower are the laticiferous ducts, the greater is the resistance to flow which must be overcome. The reason for the relatively large flow of latex upon first wounding the bark of a *Castilloa* tree (which contains relatively wide latex tubes) is thus understandable.

[157] *Kautschuk*, **3**, 95, 147 (1927). See also W. H. Arisz, *Arch. Rubbercultuur*, **12**, 220 (1928).

a short time the strips can be wound up (*see* Fig. 27). The coagulants used are discussed in a later section. In regard to the technic of the Lewa method, it may be mentioned that the cuts are about 1 cm. in width. It is preferable to have them run horizontally. Various areas (5 to 10 cm. wide and 30 to 40 cm. long) distributed over the trunk and larger branches of the tree are tapped by means of the small cuts just described. The coagulated rubber is easily removed from the bark (as long as it is not yet dry), and is usually rolled into more or less large balls. The strips of rubber are often rolled on wooden sticks of some 0.5 m. length and 5 to 6 cm. thickness or on wooden rolls of about 5 to 6 cm. diameter. When cut off from these wooden devices, the rubber can be readily separated into individual sheets. Purification of these sheets on the washing rolls is easily accomplished.

Figure 27 — Four-year-old *Manihot Glaziovii* trunk tapped according to the Lewa Method.

According to P. van Romburgh,[163] the *Ficus elastica* of eastern Asia is usually tapped by horizontal or slanting hatchet cuts, which are of different length, but which (in order to preserve the tree) must not be over 10 to 20 cm. long. The latex coagulated on the bark is scraped off after it has dried, while the latex which flows out is collected on large leaves or pieces of metal sheet.

According to E. de Wildeman and L. Gentil,[164] vine rubber is obtained in Belgian Congo by means of horizontal cuts which do not occupy more than a third of the circumference of the trunk and which are separated from each other by a distance of almost 20 cm. The rubber, which coagulates spontaneously on the bark after the tree is wounded in this manner in the morning, is collected in the afternoon or the following morning. It is then rolled

[163] *Mededeel. uit's Lands Plantentuin,* **39,** 51 (1900).

[164] de Wildeman, E. and Gentil, L., "Lianes caoutchoutifères de l'État Indepéndent du Congo," p. 151, Brussels, **1904.**

around a small stick to a spindle-like shape, or is rolled into balls. Sometimes it is cut into cubes or irregularly shaped pieces (thimbles).

Tapping by Means of Channels

In order to facilitate the collection of latex, small cuts, in the form of channels, are often made on the trunk. Tapping knives of various forms are used for this purpose. It is necessary that these instruments be provided with iron strips on the sides to prevent too deep penetration into the bark. At the suggestion of D. Sandmann, such instruments were patterned after a model made by C. Schlieper in Amani.

According to C. O. Weber,[165] the tapping of *Castilloa* trees in Colombia is accomplished by making wedge-shaped channels in the bark of the trunk with a heavy knife, 50 cm. long. This method cannot be considered to be a desirable one, however.

According to R. Henriques,[166] troughs, which reach to the top of the tree, are cut on the stem and branches of *Kickxia* trees in the vicinity of Lagos. These channels empty into a main trough on the stem (which latter in turn reaches to the base of the trunk). The latex flows down these troughs and can be collected in a vessel fastened to the lower end of the main channel. H. Bücher[167] recommended that *Kickxia* trees be tapped by means of two channels which run in the direction of the trunk and which are separated by two hand-breadths from each other.

Manihot piauhiensis, the short trunk of which is covered with hard bark, cannot be satisfactorily tapped by the usual methods. According to E. Ule,[168] this species is tapped just above the roots. A cavity is first made at the base of the trunk by removing the earth, and above this cavity (near the crown of the roots) the bark is removed with a knife, which is rounded or crumpled at the point. The latex flows into the hole and coagulates. The cake of rubber formed can be removed after two or three days. Since the rubber thus obtained is very much contaminated with sand, the surface of the hole is frequently pre-coated with a thin layer of soil, that from white ant hills being particularly suitable. The soil is easily washed from the small cakes and a reasonably pure product is obtained. After a short time, the tree can again be tapped in the same manner. In fact, no harm results from tapping it on the same side again. One man is able to tap 200 trees in this manner, his route being so arranged that each tree does not receive attention oftener than twice each week.

Tapping by Means of Channels and Small Incisions

According to the method recommended by M. K. Bamber[169] for *Hevea brasiliensis,* and by D. Sandmann for *Manihot Glaziovii* (Fig. 29), a vertical channel is made on the stem with a flat curved knife (after the preliminary removal of the hard cork layer in the case of *Manihot*). (*See* Fig. 29.) This channel serves only for the conduction of the latex, however, and is so flat that the least possible amount of latex flows out. It is from small horizontal cuts (made after the completion of the channel) that the latex flows. Several of these incisions, which are each about 1 cm. wide, are produced simultane-

[165] Weber, C. O., "The Chemistry of India Rubber," p. 23, London, **1906.**
[166] Henriques, R., "Der Kautschuk und seine Quellen," p. 19, Dresden, **1899.**
[167] *Deut. Kolonialblätter,* **Nos. 12 and 13** (1910).
[168] *Notizbl. Bot. Gart. u. Mus. Berlin,* **5,** 31 (1908).
[169] See "Rubber Industry" (ed. by J. Torrey and A. S. Manders), p. 120, The International and Allied Rubber Trades Exhibition, Ltd., London, **1911.**

ously by a suitable instrument. A metal trough, from which the latex flows into a cup placed below, serves for the collection of the latex. In order to aid the flow of latex and to prevent the stoppage of the wound, a dropping cup is placed at the upper end of the channel, and a slow stream of water or ammonia solution flows from it into the channel.

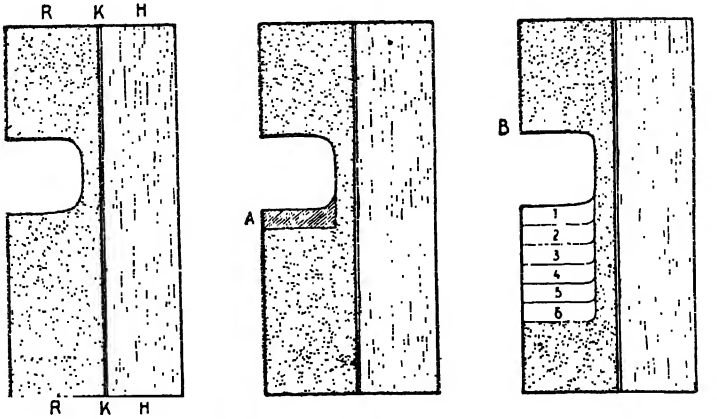


Figure 28 (Above)—Diagram of the method of paring radial cuts on the trunk.

R. Bark.
K. Cambium.
H. Wood.

I. The channel.
II. The bark strip taken off on the second tapping day (illustrated by the shaded section A).
III. The bark strips taken off on successive tapping days (marked 1, 2, 3, 4, 5, 6).

Figure 29—Trunk of a 6½-year-old *Manihot Glaziovii* tree tapped according to the Bamber-Sandmann method.

Experiments conducted by the author[170] on *Manihot* in German East Africa did not indicate that this method is a desirable one. Whether it would yield better results with old trees and under different climatic conditions is still to be tested. Moreover, the method described has not proved advantageous for *Hevea* in Ceylon.[171]

A similar method, however, seems formerly to have been advantageously used with *Ficus elastica*. For these trees it was recommended by van Gelder[172] that a system of flat channels, in which pricks are made with a knife, be produced. About half of the latex can be obtained in liquid form in this manner.

Paring Method

The paring method is now commonly in use for the tapping of *Hevea* trees on the plantations. In consideration of the great importance which *Hevea* rubber now has commercially, it should be of common interest to describe this method somewhat in detail. On account of the hard consistency of the bark this method is much less readily used with *Manihot Glaziovii*. According to P. Arens,[173] however, good results were obtained in Java by tapping *Manihot* trees according to this method. The method cannot be given consideration for species which show no marked tapping response.

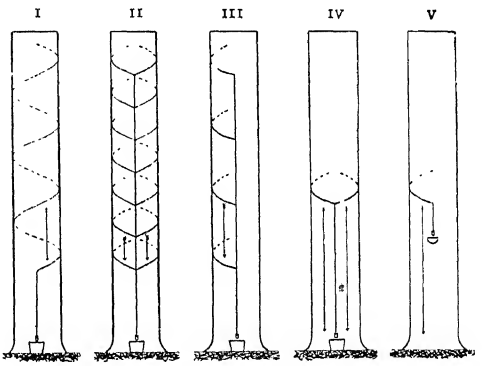


Figure 30 — Schematic representation of the various tapping methods.

I. Spiral cut.
II. Herring-bone cut.
III. Half-herring-bone cut.
IV. V-cut around the entire trunk.
V. Tapping channel around half of the trunk.

In using the paring method (Fig. 30), a vertical channel (leading channel) which leads to a point just above the ground, is first made on the trunk. With the help of a metal trough stuck into the bark, the latex flowing into this channel can be led into a collection vessel on the ground. More or less sloping channels with lower ends connected with the leading channel (so that the latex can flow down into it) are then cut in the bark. These sloping channels will be designated as tapping channels.

On the second tapping day, further channels are not made on the trunk; instead strips of bark some 1.5 mm. thick are cut from the lower edge of the tapping channels (Fig. 28). By this means the same system of latex vessels is again opened and a flow of latex is again started. On the following day another strip of bark is pared off. This process can be continued until the pared surfaces have reached the lower end of the leading channel

[170] Zimmerman, A., "Der Manihot-Kautschuk," p. 207, G. Fischer, Jena, 1913.
[171] *Rubber Res. Scheme, Bull.*, No. 71 (1918).
[172] *Tropenpflanzer*, 15, 653 (1911).
[173] *Mededeel. Proefsta. Malang*, No. 6 (1913).

and further tapping is no longer possible. When the entire available surface of the trunk is removed, the tapping can be begun again in the same manner, as soon as the bark has been regenerated sufficiently.

In going into this method more in detail, mention may be made of the fact that it can be used in various ways. Consequently, especially in earlier times, the size and direction of the channels differed greatly on the various plantations. Likewise the number of tappings made on the tree each year differs considerably.

The method to be regarded as the most rational is the one by the use of which (1) the maximum yield per single tapping is obtained, (2) the trees can be tapped the greatest possible length of time without a decrease in the yield taking place, (3) the trees are protected from injury as much as possible so that they remain productive for a long time, (4) the quality of the rubber is not impaired by continued tapping, (5) the greatest possible proportion of the latex can be obtained in the liquid form, and (6) a tapper can gather the greatest possible amount of rubber in a given period of time.

Considerations involving the channel system to be used on the trunk and the method of obtaining maximum yield for each tapping were formerly given too much weight. Frequently a channel winding in several spirals on the trunk served as a tapping channel (*see* Method I of Fig. 30). In this case all the bark on the lower part of the trunk is obviously removed, when, by paring off strips of bark, the upper edge of the next lower winding has been reached. The number of tappings possible in the first period is dependent only on the vertical distance between the individual windings. Whenever two spiral windings were used in place of one, as was also done in the early days, the number of tappings possible in the first period was only half as great.

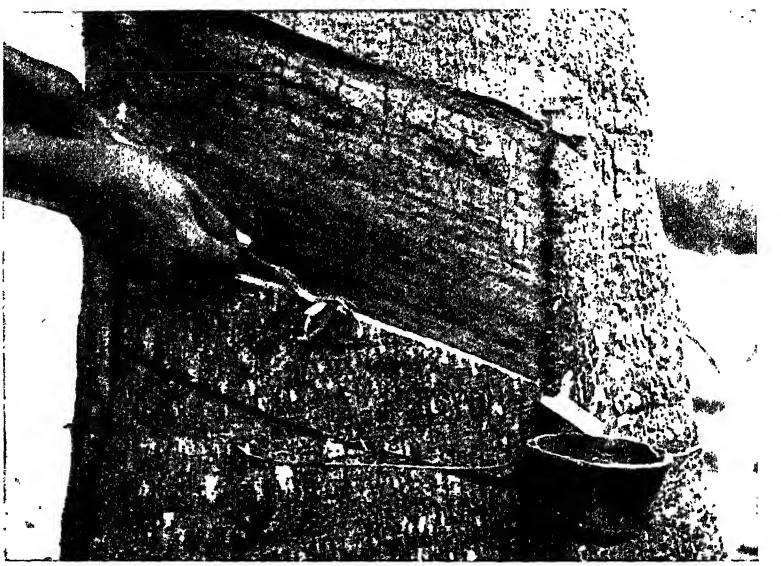


Figure 31—Paring off the bark strip in tapping ¼ of the circumference. (From the motion picture film of E. A. Hauser.)

The herring-bone cut, in which a number of tapping troughs empty into the leading (main) channel from both sides, was also very popular (*see* Fig. 30, II). In this case the number of possible tappings is dependent upon the distance between the various channels. If only three or four tapping channels are used in place of five in the same space, a considerable prolongation of the tapping period is possible. A further prolongation is obtained if, as is shown in the illustration, the tapping channels do not extend entirely around the trunk but only about half-way around, so that after one-half has been pared the other side can then be tapped. A doubling of the tapping period is thereby obtained. The same also applies to the so-called half-herring-bone cut, with which the tapping channels empty into the leading channel only from one side (Fig. 30, III). Considerably longer tapping periods are permitted by the V-cut illustrated in Figure 30, IV. The most favorable in this respect is the simple slanting cut (illustrated in Fig. 30, V), which has come into use on most of the plantations.

The photographs in Figures 31 to 33, made by E. Hauser, serve to illustrate this method. Figure 31 shows first how a strip of bark is pared from a tree which has been tapped repeatedly. It is to be noticed that in this case the collection vessel is fastened close below the tapping channel by means of a wire frame. By this expedient the amount of latex left in the leading channel is much less than is the case when this channel reaches to the ground. Figure 32 shows the latex from the wound flowing together into small drops, while in the stage illustrated by Figure 33 the entire wound is already covered with latex, which slowly drops into the collection vessel.

In connection with the merits of the different tapping systems it must be borne in mind that the latex yield is in no way proportional to the dimensions of the wound, and that twice as much rubber is not obtained from a

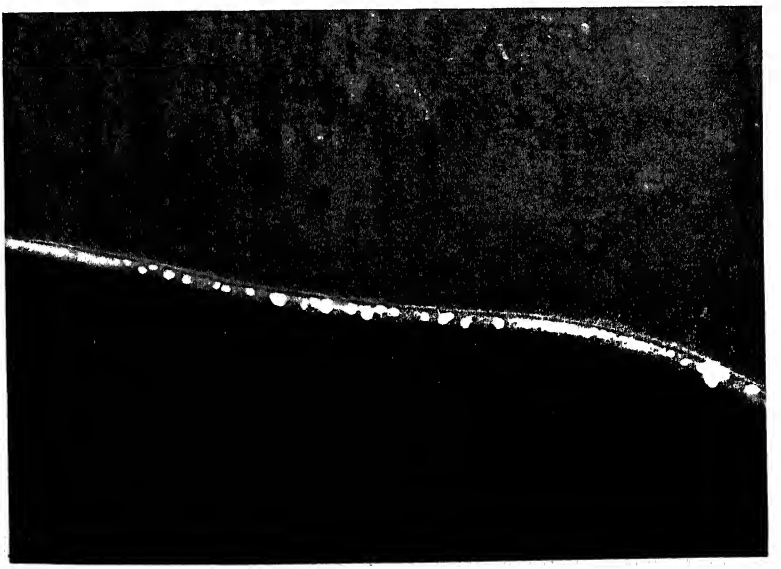


Figure 32—Beginning of the latex flow.
(From the motion picture film of E. A. Hauser.)

wound which goes entirely around the trunk as from one which goes only half way. Such a proportionality could only exist if no flow of latex took place in the transverse direction.

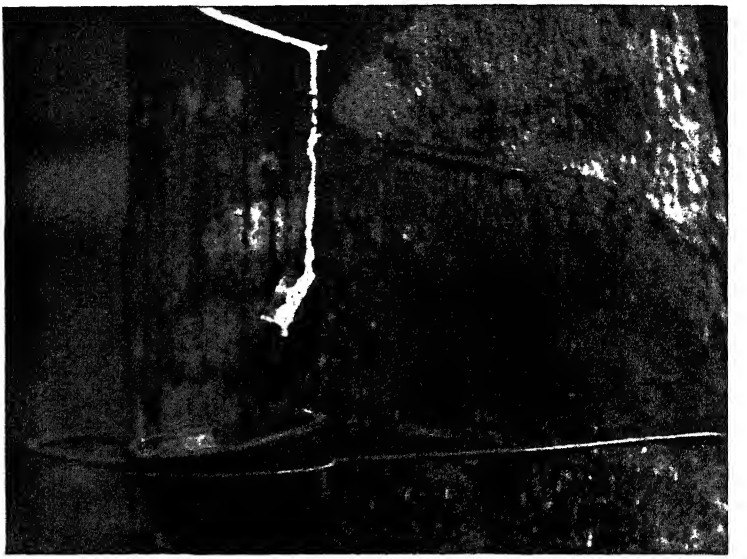


Figure 33—Latex flowing into the collection cup.
(From the motion picture film of E. A. Hauser.)

Recent economic conditions have exerted an influence on the type of tapping system used.* According to C. E. T. Mann, [*India Rubber J.*, **84**, 653 (1932)] so-called double-cut systems, which permit of a large economy in labor costs (although at the expense of a small loss in crop), have been attracting a great deal of attention. Experiments on a full spiral cut or with two "V" cuts at the same level have been tried in Malaya. A system introduced from Ceylon and commonly referred to as the Sunderland system is also being tested in Malaya. This system is characterized by a drastic tapping and a long period of recovery. The tapping cuts are laid out at different levels and tapping is repeated at intervals of three days. After tapping has been continued for from five to eight months, a rest period of equal length is provided. Very promising results are said to have been obtained thus far. It is stated that the crop does not fall below 90 per cent of that of a normal alternate-day tapping system, and that the tapping costs are reduced about one-third.

On account of the interruption to the flow of sap, the more extended the wound, the greater is the damage to the tree. With the use of extended channels and frequent tapping, the quality of the latex is also injured and the yield is decreased.

The direction of the wound on the trunk is also important from the point of view of the size of the yield to be obtained. As was explained on page 50, the latex vessels are so situated in the bark that the largest yield usually is to be obtained with horizontal cuts and the smallest with lengthwise cuts. Since the latex cannot flow downward in horizontal channels, it is necessary, in order to obtain the greatest possible amount of latex in liquid form, to

* Translator's note by V. N. M.

give the channels a certain slope. Experience has shown that an angle of about 35° with the horizontal is usually the most favorable. This angle was the basis for the construction of the systems shown in Figure 30. Since the tangent of 35° is approximately 0.7, this angle can very readily be marked on the tree by making use of a right-angled triangle so constructed (from flexible sheet metal) as to have the sides next to the right angle related to each other in length by the ratio of 10 to 7. If this triangle is placed on the tree so that the long side is horizontal and the short one is vertical, the hypotenuse indicates the desired direction.

It was shown on page 50 that larger yields are obtained from wounds which rise to the left than from those which rise to the right.

It is further to be observed that the smaller the wound produced at each tapping, the more delayed will be the time when the whole bark surface is pared off and it is necessary to begin tapping the renewed bark.

In order that a normal regrowth can take place, it is very necessary that the cambium lying between the wood and bark not be injured by the tapping, as the wood and bark cells are formed from it. An injury to the cambium causes the formation of an irregularly-shaped wound structure ("callus"). This "callus" can lead to a thickening of the bark, which (in turn) can hinder tapping of the tree. In order to prevent an injury to the cambium, it is a rule that the wound must not penetrate deeper than 1 to 2 mm. from it. If a still more shallow cut is made, a considerably smaller amount of latex is obtained, since the greatest amount of latex is found in the innermost "cylinders" of latex vessels. Deep wounds, caused by careless tapping, may be suitably closed with tree wax or paraffin, by which the healing is accelerated. According to the experiments of S. V. Simon,[174] new bark elements, as well as latex vessels which differ in no way from those in untapped bark, are formed on the pared surface within a few weeks, if no injury to the cambium has occurred during the tapping. Following this regrowth the tapping surface can again be supplied with organic nutritive material by means of conduction. In well-nourished trees, no use of the starch in the wood under the pared bark takes place. The wood cells formed during the tapping period can even be partly filled with starch, although at a slower rate than in the wood underneath the non-tapped bark. Just underneath the cork layer, which is immediately formed on the surface of the injured bark tissue, are also formed one or more layers of stone cells, which one month after tapping have already reached a considerable size and have produced an effective protection against outside influences.

N. L. Swart and A. A. L. Rutgers[175] observed that the pared bark surface was sufficiently regenerated after the first tapping to give a good yield again upon renewed tapping in about four years, or somewhat more quickly under very favorable conditions. After the second tapping, this stage is reached in about six years; and after the third, in about eight years. Therefore, if the tapping is to be uninterrupted, only a fourth of the surface of the trunk is to be removed each year for the first four years, only a sixth each year from the fourth to the tenth, and an eighth from the tenth to the eighteenth years. This system is possible only when the wound is small or the tree is seldom tapped.

The lower part of the trunk usually gives a greater yield than the higher part. The tapping is consequently begun, especially with young trees, at

[174] *Tropenpflanzer*, **17**, 63 (1913).
[175] Swart, N. L., and Rutgers, A. A. L., "Handboek voor de rubbercultuur in Nederlandsch-Indië," p. 298, J. H. Bussy, 1912.

not too great a height. The longer the tapping wound, the greater is the work of the tapper. The amount of work required is usually closely proportional to the length of the wound, but the yield does not increase proportionally. With sufficient practice, the tapper can tap most quickly when he can always perform the paring in the same direction. For example, more time is necessary for a V-cut, the arms of which each go one-fourth of the distance around the trunk, than for a single sloping cut which goes half-way around the tree. The less the tapper needs to move about in his work, the more quickly will the tapping be accomplished. Therefore all tapping surfaces are laid out in the same direction. It is also quite obvious that the tapper can tap fewer trees in the same time in young groves, where only a part of the trees are tapped, than in old ones, where all the trees are tapped.

As a rule, tapping may be begun with trunks which have a circumference of 45 cm. at a height of 70 cm.[176] This circumference is attained, under favorable conditions, by about 30 to 40 per cent of the trees on a 3½-year old plantation. Since a few selected trees cannot be singled out for tapping, only about 1 to 1½ grams of dried rubber is to be estimated from each tappable tree of this age. A tapper, therefore, will obtain only 400 grams of rubber from some 300 trees. If a day wage of 50 guilder cents and a preparation and transportation cost of 15 guilder cents is estimated, the cost of this 400 grams of rubber amounts to 65 guilder cents, which means a cost of about 30 U. S. cents per pound. With present low rubber prices, it is unprofitable to begin the tapping with such young trees. On plantations which work under still less favorable conditions, and have a higher cost of production, tapping must be begun still later.

In order to be able to estimate how many trees a tapper can tap in one day, consideration must be given to the fact that the yield is usually greatest at daybreak. Then it decreases—at least on a clear day—slowly at first, but faster from 9 o'clock until noon. During this time the amount of latex collected in the liquid form becomes steadily smaller. In the afternoon the yield increases slowly, but is still considerably smaller in the evening than in the early morning. Usually it is considered necessary that all the trees be tapped between 6 and 9:30 or 10 o'clock in the morning. The collection of the latex is then begun. In the prescribed time an experienced tapper can, by tapping with a cut which passes a third of the way around the trunk, tap about 250 trees on young plantations with some 30 to 40 per cent of tappable trees, about 200 trees on unfavorable terrain and about 350 to 400 on plantations in full production.

How often the trees are tapped during the year is naturally of great influence on the yearly yield to be obtained.* In this respect it is to be observed that a daily tapping is possible without a decrease in the yield when the wounds are not too extended. In many districts, an interruption of the tapping is necessary during the rainy season or during a severe drouth. The tree also gives proportionately little rubber at the time when the new foliage is appearing.

Apart from such interruptions, trees were formerly tapped daily on most plantations. In recent times tapping is usually less frequent. It either is done every other day, or definite rest periods are introduced in the system of daily tapping. In the year 1926, according to R. Riebl,[177] 57 per cent of the

[176] Swart and Rutgers, *loc. cit.*

[177] *Arch. Rubbercultuur*, **10**, 377 (1926).

* See translator's note on p. 78.

plantations in Java were tapped every other day, 24 per cent with a rest period of a month or less, 13 per cent daily, 4 per cent every third day, and 2 per cent with a rest period of more than a month. The length of the tapping cut was almost universally less than half the circumference of the trunk.

The thickness of the bark strip which must be pared off to open the latex vessels must be greater with long rest periods than with shorter ones, because the dried part of the bark on the wound increases gradually. For example, it has been stated that with daily tapping a bark strip 1.25 mm. thick must be taken off, whereas a 1.6 mm. strip is necessary when the tapping is on alternate days.

In order to show how tapping can be carried out continuously for 18 years on a plantation a synopsis is given of a tapping method which was designated by N. L. Swart and A. A. L. Rutgers[178] as the most profitable one. This method is based on the assumptions that a tapping surface of 45 cm. height on the average is pared off in a year, and further that four years are required for the regrowth of the bark after the first tapping round, six years after the second, and eight years after the third. The tapping wound passes one-third of the way around the trunk in all cases. In the first round (Fig. 34, I) the tapping is begun at a height of 70 cm. so that the lower, latex-rich part of the trunk is tapped. The tapping channel ends 10 cm. above the ground, so that the metal trough stuck into the trunk and the collection vessel may have a place. Three sections of the surface are arranged for the first tapping period (*A*, *B* and *C* in Fig. 34, I). Surface *A* is tapped in the

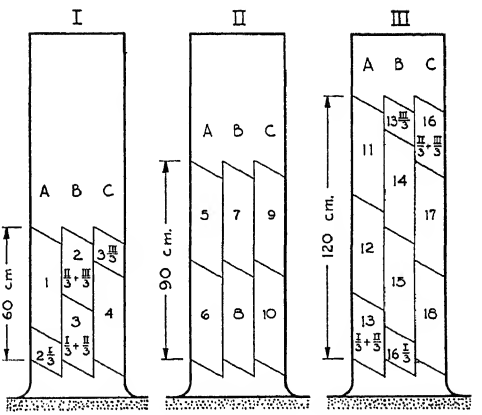


Figure 34—Tapping scheme. The surfaces tapped in the individual years are indicated on the developed surface of the trunk.

first year and the first third of the second year, surface *B* in the remainder of the second year and the first two-thirds of the third year, and surface *C* in the remainder of the third year and in the fourth year. After the expiration of this time, the bark on surface *A* is regrown so well that it can again be tapped. However, in order that there may be a longer rest period for the regrowth of the bark, the tapping is begun at a height of 100 cm. so that three surfaces 90 cm. high are involved in the second round of tapping (*A*, *B* and *C* in II). Surface *A* is tapped in the fifth and sixth years,

[178] Swart, N. L. and Rutgers, A. A. L., "Handboek voor de rubbercultuur in Nederlandsch-Indië," p. 300, J. H. Bussy, 1912.

B in the seventh and eighth years and *C* in the ninth and tenth years. At the expiration of the second round, the upper part of surface *A* has had six years for the regrowth of the bark. The third round is begun at a height of 130 cm. so that three surfaces of 120 cm. height are available. From the eleventh to the eighteenth year, surfaces *A*, *B* and *C* can be tapped in the manner illustrated in Fig. 34, III. At the expiration of this tapping period, the upper part of surface *A* has had a rest period of eight years so that the fourth round can be begun at once.

With reference to the instruments used for tapping, it should be mentioned that a great number of different (in part rather complicated) instruments have been made for the production of the channel and for the paring off of the bark strip. These tools are designed to make possible the quickest work and at the same time to prevent too deep penetration of the cut. In actual practice, a relatively simple instrument is generally used.

Formerly glass or porcelain collection vessels were commonly used. Aluminum cups, which, although more expensive, have the advantage that they are less readily broken and are also much lighter (so that they can be brought to the factory each day and cleaned), have recently come into favor. Glass and porcelain cups must always be kept as clean as possible in order to prevent the collection in them of putrefied rubber scrap, which can cause complete coagulation of the latex. In order to prevent infection of the bark it is recommended (especially for infected plantations) that the tapping instruments be sterilized before use. Mercuric chloride is not recommended for this purpose. Creolin is recommended as a disinfectant by P. Arens.[179]

In order to prevent the overflow of latex from the tapping channel, Watson[180] recommended that the bark just beneath it be coated with a non-wettable material, vaseline or the like.

Many anti-coagulants are used to prevent premature coagulation. These are usually added to the latex in the collection vessel, although they are frequently placed in the cup before tapping and are sometimes even painted on the tapping channel. Sodium sulfite, soda and formalin have proved especially useful for this purpose. In the case of sodium sulfite, a solution containing 10 grams of anhydrous or 20 grams of the crystalline salt in 100 cc. of water is prepared. Enough of this solution is poured into the collection vessel to give 6 cc. in each liter of undiluted latex. The sodium carbonate solution, when used, is made up to contain 10 grams of the anhydrous or 27 grams of the hydrated salt in 100 cc. of water. One per cent by volume is added to the latex. In the case of formalin, a solution containing 25 cc. of commercial formalin in 1 liter of water is prepared, and 20 cc. of this solution is added to a liter of latex.

An addition of sodium carbonate is especially recommended when the water used with the latex is rich in lime. The addition of this agent or of sodium sulfite will improve the physical properties of the rubber. Formalin, in the stated amount, is without influence but in larger amounts can cause injury.

Formerly a so-called dropping vessel (drip tin) from which pure water or dilute ammonia solution slowly dropped, was placed at the upper end of the leading channel in order to prevent premature coagulation of the latex. It was believed that the stopping of the latex flow was delayed and a greater amount of latex could be obtained. This assumption was not confirmed by

[179] *Mededeel. Proefsta. Malang*, **25**, 6 (1919). [180] *India Rubber J.*, **72**, 818 (1926).

the investigations of P. Arens,[181] however. At the present time the dropping vessel is scarcely ever used.

Combined Paring and Pricking Method

In the use of this method the procedure at first is the same as with the previously described paring method. In order, however, to open the deeper-lying latex vessels and to cause the latex in them to flow, a suitable instrument (pricker) is stuck into the bark, after the removal of the bark strip, which is scraped off less deeply to prevent injury to the cambium. A wheel, which is provided on its circumference with sharp teeth 10 mm. long and 5 to 8 mm. wide, is used for this purpose. In later tapping, a new bark strip is scraped off and the pricker is stuck into the bark thus laid bare.

The method described can, when appropriately used, give somewhat higher yields than the straight paring method. The use of prickers, however, causes considerable injury and interferes with the regrowth of bark.[182] Its use appears to be quite limited at the present time.

The Direct Application of Latex

Although it has long been known that latex collected from the rubber tree could be used directly for the manufacture of technical articles, especially waterproof material; and it was proved by Fourcroy in 1791 that latex could be kept liquid for a long time by the addition of alkali; and patents on the manufacture of rubber articles from latex were taken out in the years 1791, 1824 and 1825,[183] only a very small amount of latex (and that mostly for scientific research) had arrived in the countries producing rubber goods up to the year 1920. Since about 1920, industry has shown an ever-increasing interest in the direct use of latex.* It follows from the fact that the amount exported from the Middle East in the last few years has already assumed considerable importance that latex is no longer used only for small experiments. This is apparent from Table 4, taken from the Bulletin of the Rubber Growers' Association:

TABLE 4.—*Exports of Latex in 1,000 (Imperial) Gallons.*

	1923	1924	1925	1926	1927	1928	1929	1930	1931
Malaya	74	715	2,315	2,088	1,561	919	1,708	815	752
Ceylon	11	59	4	13	0.3	0.7			
Sumatra	1,499	644	1,433	28	54	933	833	1,699	2,443
Total	1,584	1,418	3,752	2,129	1,615.3	1,852.7	2,541	2,514	3,195

Until recently latex was always shipped with its naturally occurring water, or even somewhat diluted with water (whereby its transportation

[181] *Arch. Rubbercultuur*, **3**, 36 (1919).
[182] *Rubber Res. Scheme, Bull.*, **69** (1918).
[183] Cf., Hauser, E. A., "Latex," pp. 5 & 7, Th. Steinkopff, Dresden and Leipzig, **1927**.

* Translator's Note. The developments in the direct use of latex during the 5-year period following the publication in 1927 of Hauser's book on "Latex" have been recently reviewed by V. N. Morris and H. W. Greenup, *Ind. Eng. Chem.*, **24**, 755-770 (1932). This review covers such fields as scientific investigations of latex systems, preservation and shipping, concentration of latex, incorporation of compounding ingredients, manufacture by dipping, spraying, molding, electrodeposition, etc., and uses for and products from latex. The reader is also referred to the articles by D. F. Twiss, F. W. Warren, and J. H. Carrington, *Trans. Inst. Rubber Ind.*, **6**, 419-452 (1931), by R. G. James, *Ibid.*, **9**, 42 (1933), and by D. F. Twiss, *J. Soc. Chem. Ind.*, **52**, 410 (1933), on the subject of the direct use of latex, and to the bulletin, "Rubber Latex," by H. P. Stevens and W. H. Stevens, issued by the Rubber Growers' Association in 1933. V. N. M.

cost is increased). A process by which latex can be converted into a concentrated form without the physical properties of the rubber being injured, has been sought during the past few years. A pasty mass which does not need an air-tight container for shipping, and can, by dilution with water, be converted into an emulsion or suspension similar in all essential properties to fresh latex, is now made from latex. Further, it is possible to vulcanize the rubber in the latex without causing visible change.

The discussion of the applications of liquid latex can be separated into five different sections; the uses of ordinary liquid latex, the concentration of latex, the vulcanization of latex, the incorporation of compounding ingredients in latex, and methods for the practical utilization of compounded latex.

Liquid Latex

Preservation with Ammonia

The spontaneous coagulation which tends to occur in Hevea latex after a short time must be prevented by the addition of a preservative, if the liquid state is to be retained. In practice, ammonia is used almost exclusively for this purpose. For the preparation of a uniform, standard product, it was recommended by O. de Vries [184] that the latex be diluted to a water content of 75 per cent, and that 5 grams of ammonia be added for each liter. The addition of ammonia is made as soon as possible after the collection of the latex. Petroleum cans, as well as iron drums and tanks, are used for shipping. According to O. de Vries and N. Beumée-Nieuwland,[185] the ammonia content of preserved latex remains constant when the latex is kept in well-closed containers and the alkalinity is so great that no bacterial decomposition can take place. With less alkalinity (0.1 *N*, for example) spontaneous coagulation can set in, whereby the alkalinity is decreased as the ammonia is combined with the resulting acid.

If ammonia-preserved latex is permitted to remain undisturbed in a closed vessel for some time there occurs a separation into layers to some extent. The rubber content is least in the lowest layer. In the upper creamy layer, in which some of the rubber particles may become bound together upon long standing, the rubber content may amount to as much as 76 per cent by weight. According to O. de Vries and N. Beumée-Nieuwland,[186] this cream contains only a small amount of serum constituents. After dilution with water it is more difficult to coagulate with alcohol than fresh latex of the same concentration. Coagulation of this cream takes place readily upon the addition of a small amount of common salt. The diluted cream is also readily coagulated by acetic acid. The yellow rubber obtained from the cream contains little nitrogen, but the ash is approximately normal. The sheets obtained by the drying of cream show a tendency toward tackiness.

According to C. Beadle and H. P. Stevens,[187] the ammonia is completely separated from preserved latex by dializing the latter for two to three days with frequent changes of water. The latex so obtained ex-

[184] *Arch. Rubbercultuur*, **7**, 168 (1923).
[185] *Arch. Rubbercultuur*, **11**, 371 (1927).
[186] *Arch. Rubbercultuur*, **11**, 295 (1927).
[187] *Kolloid-Z.*, **13**, 211 (1913).

hibits a normal behavior at first, and is coagulated normally by acid. Soon, however, aggregates of rubber particles are formed, and after some days the effect of acids is not to coagulate but merely to cream the latex.

That various changes take place in ammonia-preserved latex follows from the fact that sediment usually separates from it. In experiments carried out at the Imperial Institute,[188] on two samples of such a sediment, the following analytical results were obtained:

	Per Cent
Rubber	30
Acetone extract	11.6 and 6.4
Nitrogen-containing material (insoluble in acetone)	2.4 and 1.6
Fe_2O_3	9.0 and 15.1
MgO	16.0 and 13.1
P_2O_5	28.0 and 23.6

Traces of K, Si and Sn were also found to be present. The iron and tin found in the sediment may have been obtained from the container.

O. de Vries and N. Beumée-Nieuwland[189] found in such a sediment:

	Per Cent
Rubber	22
Magnesium ammonium phosphate	30
Proteins, impurities, etc.	1
Ash, besides NH_4MgPO_4	4.5
Water, ammonia, and other liquid constituents	37

In ammonia-preserved latex there take place decompositions of the proteins and other changes (of a nature not yet determined with certainty)[190] which exert a great influence upon the rate of vulcanization and the viscosity of solutions of rubber obtained from it. It was shown by O. de Vries, R. Riebl and N. Beumée-Nieuwland[191] that the rate of vulcanization of rubbers obtained from latices preserved with ammonia for different lengths of time increases at first, later decreases, reaches the original value after a month, reaches a minimum after two months, and then again increases. The viscosity of the rubber solutions decreases in the first stage, rises considerably in the second, and in the third period again decreases. The mechanical properties of the rubber obtained from ammonia-preserved latex do not differ greatly from those of normal Hevea rubber, according to experiments conducted at the Imperial Institute.[192] O. de Vries and N. Beumée-Nieuwland[193] obtained similar results, and were also able to determine that rubber obtained by coagulation from ammonia-preserved latex had not become tacky after being preserved for years.

Other Preservatives

The attempt of B. J. Eaton,[194] T. E. H. O'Brien,[195] O. de Vries,[196] and others to find preservatives which would show to advantage in comparison with ammonia has not as yet shown results utilizable in practice. Formaldehyde has been used repeatedly in laboratory experiments

[188] *Bull. Imp. Inst.*, **22**, 139 (1924).
[189] *Arch. Rubbercultuur*, **11**, 314 (1927).
[190] Cf. Hauser, E., "Latex," p. 107, Th. Steinkopff, Dresden and Leipzig, **1927**.
[191] *Arch. Rubbercultuur*, **9**, 345 (1925) and **11**, 325 (1927).
[192] *Bull. Imp. Inst.*, **22**, 138 and 140 (1924).
[193] *Arch. Rubbercultuur*, **11**, 325 (1927).
[194] *Bull. Imp. Inst.*, **21**, 393 (1923).
[195] *Ibid*, **22**, 220 (1924) and *Rubber Res. Scheme, Bull.*, **32**, (1924).
[196] *Arch. Rubbercultuur*, **10**, 149 (1926).

for the preservation of samples of latex. According to C. Beadle and H. P. Stevens,[197] about 20 to 30 cc. of 40 per cent commercial formalin should be added to a liter. They found, however, that in the preserved latex the rubber particles come together into aggregates of different sizes, of which only a few if any show Brownian movement. They found further that the larger the aggregates the greater was the tendency for creaming to occur. The smaller aggregates remain suspended in the serum, and it is not possible to separate the cream from free or slightly aggregated particles by repeated dilution with water, shaking in a separatory funnel and drawing off the milky liquid. The larger aggregates cannot be split up into the original particles.

In latex preserved with formalin chemical processes also take place. According to C. Beadle and H. P. Stevens,[198] a quantity of acid as great as or greater than that necessary for the coagulation of fresh latex is generated therein. Usually coagulation cannot be brought about by the further addition of acid. Whether this coagulation takes place or not depends upon the content of free rubber particles, since they alone are influenced by the action of the acid. Further addition of acids or of salts usually results only in creaming.

That the physical properties of the resulting rubber are always lowered as a consequence of preservation of the latex with formalin was reported by O. de Vries,[199] R. Ditmar,[200] and E. Hauser.[201]

Sodium hydroxide can also be used for the preservation of latex, but, according to the experiments of T. E. H. O'Brien[202] and O. de Vries and N. Beumée-Nieuwland,[203] it shows no advantage over ammonia. Products made from latex so preserved show a tendency towards tackiness.

The recent investigations of H. Freundlich and N. Talalay* [*Kautschuk*, **9**, 34, 49 (1933)] have demonstrated that the catalytic oxidation of rubber in the presence of copper is greatly accelerated when sodium hydroxide is present in the latex.

Concentration of Latex

The four different methods suggested for the concentration of latex will be described in the sections which follow.

Creaming of Latex

According to the process suggested by J. Traube,[204] 60 to 70 cc. of latex is mixed with a 10 per cent aqueous solution of Carragheen moss and the mixture is heated for a long period at 40 to 60° C.† This treatment causes a separation into two layers differing in rubber content. In the lower layer a certain percentage of rubber still remains. The upper layer, a cream rich in rubber, remains liquid, and is relatively unstable, so that it must be mixed with a preservative such as ammonia and be

[197] *Kolloid-Z.*, **13**, 207 (1913).
[198] *Kolloid-Z.*, **13**, 211 (1913).
[199] de Vries, O., "Estate Rubber," p. 85.
[200] *Gummi-Ztg.*, **41**, 1688 (1927).
[201] Hauser, E., "Latex," p. 111, Th. Steinkopff, Dresden and Leipzig, **1927**.
[202] *Bull. Imp. Inst.*, **22**, 221 (1924).
[203] *Arch. Rubbercultuur*, **9**, 694 (1925).
* Translator's note by V. N. M.
[204] *Gummi-Ztg.*, **39**, 434 (1925) and *Kautschuk*, (October) 13 (1925).

† Translator's Note. According to the patent literature, other substances which facilitate separation of the rubber globules in latex include glue, gelatin, Iceland moss, Irish moss, pectin, gum arabic, Karaya gum, alginic acid, and various alginates. See Banks, U. S. Pat. 1,755,379 (1930); Jackson, Brit. Pat. 294,002 (1928); K. D. P., Ltd., Brit. Pat. 337,269 (1930); McGavack, U. S. Pats. 1,647,805 (1927) and 1,740,994 (1929); Smith, U. S. Pat. 1,678,022 (1928). V.N.M.

packed in a water-tight container for transporting. This method of concentration has been used but little in practice. The same applies to the process suggested by O. de Vries and N. Beumée-Nieuwland,[205] according to which creaming is caused by the addition of a considerable quantity of sodium hydroxide. The cream thus obtained possesses the disadvantage that products made from it tend strongly toward tackiness.

Centrifuging

A complete separation of rubber particles and serum cannot be obtained by centrifuging. As was pointed out by Utermark and others,[206] it is possible to separate latex into a cream rich in rubber and a "skim milk" poor in rubber, by means of a rapidly rotating centrifuge. H. N. Bloomendaal and N. H. van Harpen,[207] using an apparatus constructed by the Alpha-Laval Company, obtained a 60 per cent rubber cream and a 5 per cent "skim milk." The concentration of the cream can be carried still further by the addition of protective colloids. Rubber from the cream has a very yellow color and contains only small amounts of protein and other serum constituents. A still more complete concentration is attained if the cream is again centrifuged after the addition of water. This absence of serum constituents causes the rubber to be non-hygroscopic, which may be advantageous in certain applications, especially in the electrical industry. The 5 per cent "skim milk" is readily coagulated. The cream is still so liquid when it has a rubber content of 60 to 70 per cent that it can be pumped very well. Some observations on the properties of rubber from the cream were reported by O. de Vries and N. Beumée-Nieuwland.[208] To what extent the Utermark method will prove to be profitable in practice cannot yet be determined with certainty.*

Incidentally, at this place may be mentioned the supposition of investigators at F. R. Henderson and Company, Inc.[209] to the effect that the method of partial centrifuging could perhaps be used to separate the non-rubber material from latices of lower quality.

Filtration

With the use of certain ultrafilters, it is possible to separate rubber rom latex in an almost pure form. However, the apparatus recommended for this purpose appears to be too complicated to be used on a arge scale as yet.[210]

Revertex Process

According to E. Hauser,[211] Revertex (contraction of the words "reersible" and "latex") is prepared according to the procedure described elow. The latex is freed of impurities and coagulated lumps by screening as soon as possible after collection and, after the addition of a preervative, is kept in a large vessel until used. The protective colloid is

[205] *Arch. Rubbercultuur*, **9**, 748 (1925).
[206] *Chem. Age*, **11**, 331 (1924); also see *India Rubber World*, **68**, 704 (1923).
[207] *Arch. Rubbercultuur*, **11**, 573 (1927).
[208] *Arch. Rubbercultuur*, **11**, 382 (1927).
* Translator's Note. At the present time (1933) centrifuged latex is a commodity readily obtainable on the market. That it is finding practical application is evidenced by the statements of Carrington and others [*Inst. Rubber Ind., Trans.*, **6**, 438 (1931).] H.W.G.
[209] *India Rubber World*, **68**, 724 (1923).
[210] See Hauser, E. A., "Latex," p. 120, Th. Steinkopff, Dresden and Leipzig, **1927.**
[211] *Kautschuk*, **3**, 4 (1927).

added shortly before the latex is placed in the evaporator (Fig. 35). This latter consists essentially of a rotating hollow cylinder, which is surrounded by another cylinder and is heated by means of hot water flowing between the cylinders. From the body of the latex (which fills only a portion of the cylinder) a thin layer is taken up on the heated wall during the rotation. This layer is concentrated by evaporation and is returned to the latex as the revolution is completed. A constant mixing and a destruction of incipient foam is accomplished by a freely rotating cylindrical roll, which is within the rotating drum and which is set in motion by the latter. A stream of cold air is blown through the drum to carry out the water vapor and also to prevent the thin layer removed for evaporation from forming a skin. The evaporation is continued until the latex assumes a pasty consistency, which is attained when the water content is 20 to 30 per cent. The operation of the apparatus is then discontinued and the concentrated latex is drained into a collecting vessel. After cooling, the Revertex can be drawn off into Venesta cases (thinly coated with paraffin), in which it is shipped.*

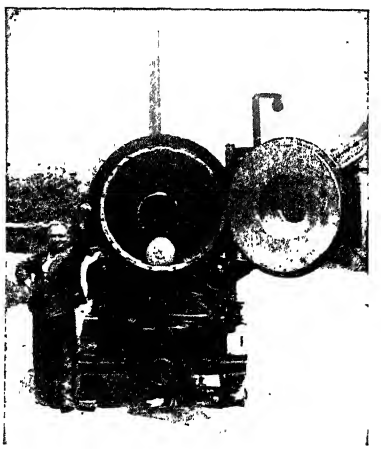


Figure 35—Transportable evaporation apparatus for the manufacture of Revertex.

(According to E. A. Hauser.)

To what extent Revertex will find application in the rubber industry in place of ammonia-preserved latex and crude rubber is not readily apparent at this time. According to statements of E. Hauser, which are disputed by various authors in many details, Revertex seems to possess important advantages.

It was first emphasized by Hauser that Revertex can be brought to any desired concentration before use by dilution with water. Since the protective colloid added for stabilization is water-soluble, it can, when necessary, be removed by a simple washing process. The behavior of Revertex toward coagulants is similar to that of fresh latex. Moreover, the rubber particles in Revertex exhibit the same constitution as those in fresh latex, while those in ammonia-preserved latex are always more or less strongly agglomerated. In contrast to ammonia-preserved latex, Revertex is distinguished by a high stability to temperature fluctuations,

* Translator's Note. All of the Revertex which has come to the attention of the translator during the past few years had been shipped in metal drums. V. N. M.

further evaporation, pressure and to friction. No coagulation is to be feared upon passage through a colloid mill. The use of Revertex is further promoted by the fact that mixtures made with it generally vulcanize in a considerably shorter time than do mixtures made with sheets or crepe rubber. The explanation of this phenomenon lies in the fact that natural accelerators are contained in Revertex* (see p. 303). Since Revertex is neither exposed to high temperatures nor caused to undergo changes through the action of strong chemicals during its manufacture, it is conceivable that the activity of these accelerators remains. Hauser considers Revertex to belong to the class of most rapidly vulcanizing rubbers. Since the rubber in mixtures made from Revertex has experienced less working than that in mixtures made from crude rubber, it is not to be wondered that the physical properties of Revertex vulcanizates are superior. The permanent set of Revertex products is usually a little higher than that obtained with plantation rubber, and tests of tear resistance and tensile strength show a superiority for Revertex over other kinds of rubber. With respect to aging, it also appears significant that the non-rubber constituents of latex remain unchanged in Revertex. Artificial aging tests have shown rubber from Revertex to possess a considerable superiority over plantation rubber.

According to E. A. Hauser, the application of Revertex, completely dispersed by addition of water, is possible wherever preserved latex has formerly been used. For many purposes the Revertex paste can be used directly, as, for example, for coating fabrics, for the manufacture of dipped goods and, especially, for the production of filler-free rubber sheets. The process of dissolving the rubber and recovering the solvent, necessary when rubber cements are used in the manufacture of numerous articles, is unnecessary when Revertex is substituted for the cements. On account of the high rubber content of the mixture, quite a thick layer of rubber can be applied. The aqueous dispersion penetrates a suitably pre-treated fabric better than does a benzene solution of rubber. Various articles, such as automobile inner tubes, may be made by spraying a suitable mixture on heated hollow forms and later vulcanizing the sprayed layer.

A novel evaporation process† has recently been patented by the Metallgesellschaft Aktiengesellschaft [Brit. Pat. 382,235 (1933)]. According to this process, latex, heated by steam or hot water to a temperature of about 90° C., is introduced through a suitably designed nozzle into an evaporation chamber in which a reduced pressure (70 mm. of mercury or less) is maintained. Since the boiling point corresponding to this pressure is about 46° C., the temperature of the latex rapidly falls to about 46° as the latex enters the chamber. The resulting evaporation of water from the latex reduces the water content of the latter by about seven per cent. The process must be repeated if further reduction in moisture content is desired. In order to produce a concentrated material with a total solid content of 75 per cent, for instance, it is necessary to repeat the operation of heating and cooling in vacuo about eleven times. If a wider range of temperatures is adopted, the number of repetitions needed to obtain a predetermined concentration is correspondingly less.

Vulcanization of Latex

The vulcanization of the rubber particles contained in latex may be accomplished by a patented process discovered by P. Schidrowitz. The suspension manufactured in this way is designated as "Vultex" (con-

* Translator's Note. The potassium hydroxide present as preservative probably also influences the rate of vulcanization. V.N.M.

† Translator's note by V. N. M.

traction of the words "vulcanized" and "latex"). The designation "Vulpro" is used to some extent for products manufactured from it.

Vultex consists of a dispersion of vulcanized rubber particles in unchanged serum.[212] The rubber particles in it exhibit a somewhat faster Brownian movement than those in fresh latex. That the rubber particles in the latex are actually vulcanized may be concluded from the changed shape of the particles, from their increasing solidity toward the inward part of the particle, from their indifference toward solvents, and from their increased negative charge. H. Green[213] established by microscopical investigation in ultra-violet light that during the vulcanization the kernel of the particle enters into a reaction with the sulfur while the hull is not influenced.

A vulcanization of the rubber particles takes place in Revertex just as in fresh or preserved latex. The product obtained is designated as "Revultex." It is stable, on account of the protective colloid contained in it, and can be diluted like Revertex.

Sulfur (in all forms) and polysulfides can be used as vulcanizing agents in the manufacture of Vultex and Revultex. The vulcanization can be effected with or without pressure at 100° C. or lower temperatures. Under favorable conditions and with suitable accelerators satisfactory vulcanization can be effected at 4° to 10° C. in as little as 24 hours, or correspondingly more rapidly at higher temperatures. In practice, however, the latex is usually heated to 70° to 80° C. with the addition of accelerators, and a complete vulcanization is obtained in 2 hours.

In spite of the fact that they are completely vulcanized, such mixtures have a very low vulcanization coefficient. The quantity of combined sulfur in Vultex products never amounts to more than 3 per cent.

A further advantage of the Vultex process is that the excess of sulfur remaining in the latex can be separated by a simple settling process. In the manufacture of Revultex this is not possible. By a suitable modification of the vulcanization process it is possible, with the use of Revertex, to obtain a paste in which no excess sulfur remains, so that it can be used in all concentrations without further treatment.

By evaporation of the water from Vultex, an insoluble film of vulcanized rubber of high quality results. In regard to the sticking together of the rubber particles, it was explained by Hauser that "a substance present in the serum shows adhesive properties in the moist condition (so that it works as a cement in the film formation). This property is lost on further dehydration and is not regained on addition of water."

By changing the length of time of vulcanization, the temperature used, the amount of sulfur added, the accelerator and activators, etc., the degree of vulcanization, elasticity, tensile strength, etc., can be varied in the manufacture of Vultex and Revultex, just as they are in the manufacturing of products from crude rubber. The process permits the use of dyes and filler pigments which could not be used in former manufacturing processes on account of their instability to heat and vulcanization. The mixing of latex with these ingredients requires practically no power, and the rubber is in no way injured. In the spreading process, it is only

[212] *Cf.* E. Hauser, *Gummi-Ztg.*, **40**, 1357 (1926) and "Latex," p. 126, Th. Steinkopff, Dresden and Leipzig, **1927**; also Schidrowitz, *Gummi-Ztg.*, **41**, 817 (1927) and *Ind. Eng. Chem.*, **16**, 1147 (1924).

[213] *India Rubber World*, **72**, 720 (1925) and *Ind. Eng. Chem.*, **17**, 802 (1925).

necessary to evaporate the water; and consequently the fabric cannot be injured by any subsequent vulcanization. Vultex and Revultex offer many advantages in the manufacture of numerous rubber articles. The physical properties of products made from Vultex, especially their aging qualities, are said to be very good. It is worthy of note that the "Vulpro-articles" have found increasing sale as well as general recognition in England.

Incorporation of Compounding Ingredients in Latex *

Although the incorporation of compounding ingredients in latex was not discussed in the German version of this book, it seems well worth while to give some consideration to this very important factor in connection with the direct use of latex. Especially is this true inasmuch as considerable literature on the subject has made its appearance since the publication of the German edition.

The introduction of compounding ingredients, or pigments (to use the term of the rubber technologists), is, in the case of latex, a fundamentally different process from that with crude rubber. According to various investigators, the difficulties with compounding ingredients for latex can be attributed to electrical charge (e.g., magnesium oxide will discharge and coagulate the negative latex particles); dehydrating power (e.g., carbon black); tendency to settle out; and failure to be wetted by latex. A procedure which lessens one of these difficulties may often aggravate another. In their recent review of the subject of the direct use of latex, the translators [214] have stated that passage of the pigment suspension, or of the compounded latex, through a colloid mill, or through a paint mill, will usually improve dispersion and retard settling, but may greatly increase the tendency towards coagulation.

H. P. Stevens and W. H. Stevens [215] state that most fine powders, when stirred into latex, coagulate it, the coagulation manifesting itself either as a sudden or a gradual stiffening of the paste. The best method of introducing pigments is to put them into the form of a paste with water, or with an alkaline solution, before stirring them into the latex, according to these investigators. Despite these precautions, the incorporation of certain pigments, such as carbon black and zinc oxide, is very difficult, and resort to the use of protective colloids is necessary. Stevens and Stevens mention hemoglobin, soap, glue, and gelatin solutions in this connection. Casein, gum tragacanth, gum ghatti, potassium soap, and saponin are included among the agents which the translators have used successfully. A certain specificity has been observed in the protective influence which the various colloids exert on the different pigments, an effective agent for one pigment not necessarily being of much service for another.

There have been several proposals for handling carbon black, which is probably the fine powder most difficult to incorporate in latex. It is reported that the use of saponin in a carbon black-water paste facilitates wetting and aids in the subsequent mixing of the paste with latex. The recent suggestion of C. R. Park [216] for increasing the dispersibility of carbon black in latex is to treat the black with the vapors of a material such as pine oil or petroleum distillate.

Several novel suggestions for facilitating the introduction of sulfur, the large particle size of which is ordinarily objectionable, have been made. According to the experience of the translators, the grinding of this pigment in a ball mill in the presence of protective colloids is probably the method having the greatest general utility. For certain purposes, sulfur may be advantageously introduced into latex in the form of the hydride, or of a polysulfide, such as ammonium or calcium polysulfide.[217]

The methods employed for the introduction of water-insoluble accelerators into latex are the same in general as those which apply in the case of inorganic compounding ingredients. Since water-soluble accelerators can be mixed with latex very readily (provided they are not of such a nature as to coagulate the latter), it is often desirable to use this type. Since latex articles are normally formed to shape and therefore do not require any further processing, such as milling or calendering, the field of applicability of ultra-accelerators is much greater than is the case with articles made from crude rubber.

* Translator's note by V. N. M.

[214] See Morris, V. N., and Greenup, H. W., *Ind. Eng. Chem.*, **24**, 755 (1932).

[215] Bulletin of the Rubber Growers' Association on "Rubber Latex," p. 35, **1933.**

[216] Canadian Pat. 309, 276 (1931).

[217] See Stevens and Stevens—Bulletin of the Rubber Growers' Association on "Rubber Latex," p. 45, **1933.**

According to Jacobs,[218] Naunton,[219] and others, almost any dyestuff carrying a negative charge may be used for coloring articles made from latex, provided the latter is vulcanized at or near ordinary temperature by the use of ultra-accelerators. Insoluble dyes may first be run through a colloid mill with a protective colloid, or dissolved in a suitable organic solvent and the solution then emulsified. In using vat dyes, it is necessary to agitate the mixture of latex and the leuco compound while exposed to the air. It is possible to use lakes, provided they are in a fine state of subdivision.

Waxes, oils, resins, and bituminous materials are in general neither soluble in water, nor can they be introduced in the form of a suspension of fine powder. Emulsification is the usual expedient employed, the non-rubber constituents of the latex sometimes serving as the emulsifying agent. Among other agents which have been used by a number of investigators for this purpose may be mentioned Karaya gum and saponin. Worthy of mention is W. A. Gibbon's[220] suggestion for adding stearic acid to latex by first forming ammonium stearate and stirring in the latter.

A method of introducing compounding ingredients, which is feasible for latex but not for crude rubber compounding, is to form the ingredient in the latex (or in water immediately before addition to the latex) by a double decomposition or similar reaction between two soluble substances. An example of a very useful reaction of this type is that between barium sulfide and zinc sulfate, in which both products formed are insoluble and of interest as rubber pigments. In this connection American and English interests[221] have patented processes for the production of such ingredients as silicic acid, various silicates, cadmium and other sulfides, barium sulfate, lithopone, calcium oxalate, and calcium and other carbonates by this method. Exceptionally good mechanical properties have been claimed for products containing pigments formed in this manner.

Keeping the pigments in suspension after they have once been satisfactorily dispersed in latex is often quite a problem. The use of latex thickened by concentration (Revertex, for instance) reduces the tendency towards the sedimentation of compounding ingredients. In employing Revertex, which is a comparatively viscous paste, the pigments may be incorporated either as dry powders or as pastes in a mixer of the Werner-Pfleiderer type. A brush-sieve arrangement, operating simultaneously with the blades of the mixer, is recommended for the introduction of dry pigments. When a high proportion of compounding ingredients is to be introduced, extra water, or a solution of alkali or of casein, should be added continually during mixing to prevent coagulation.

Certain methods for thickening normal latex (without concentrating) and thus retarding the settling of fillers have been proposed. Thus Hauser[222] suggests using the thixotropic properties of bentonite clay or other substances, Wescott[223] suggests the use of a zinc oxide-hemoglobin gel, and Teague[224] has made use of ammonium soaps of higher fatty acids for this purpose.

Methods for the Practical Utilization of Compounding Latex*

Since the recently developed methods for the utilization of compounded latex often hold much of scientific interest, and the books on the technology of rubber have heretofore not covered the matter thoroughly, it has occurred to the translators that a discussion of the subject at this point would be thoroughly justified. The methods used for the conversion of the latex mixture into the shaped but unvulcanized (unless Vultex is used) article include dipping, deposition from aggregated latex, electrodeposition, spraying, gelling and molding, and extruding.[225]

Dipping. The alternate dipping of a non-porous mold in latex and the drying of the deposited layer probably constitutes the simplest method for the manufacture of articles from latex. Products made in this manner have found increasing use and are, at present, competing very successfully with goods made by dipping in rubber cement. Included among the articles made by this method may be mentioned finger cots, druggists' sundries, balloons, coated screens, surgeons' gloves, and electricians' gloves.

Much investigation during the past few years has been devoted to the problem of increasing the thickness of the film obtained by a single dip, or decreasing the time necessary between dips. Among the methods suggested for these purposes may be mentioned

[218] *Rev. gén. caoutchouc*, **7**, No. *63*, 31 (1930).
[219] *Rubber Age (London)*, **9**, 256 (1928).
[220] U. S. Pat. 1.798.253 (1931).
[221] K. D. P., Ltd., Brit. Pat. 262,487 (1927); Dinsmore, U. S. Pat. 1,712,333 (1929); Murphy, Niven, and Twiss, Brit. Pat. 338,975 (1931).
[222] Brit. Pat. 342,469 (1931).
[223] Brit. Pat. 301,077 (1929).
U. S. Pat. 1,634,124 (1927).

* Translator's note by H. W. G. and V. N. M.

[225] Translator's Note. The patent literature with respect to these methods is thoroughly reviewed in F. Marchionna's book, "Latex and Its Industrial Applications" (The Rubber Age Publishing Company, New York, **1933**), a copy of which has just come to the attention of the translators.

concentration,[226] thickening,[227] and dipping with accompanying, or subsequent coagulation. The interesting proposal of Pestalozza[228] for facilitating the production of rubber articles by dipping involves the use of heat-sensitive latex prepared by adding solutions or suspensions of salts of bi- or trivalent metals. When a heated form is introduced, the latex adjacent to it is heated and coagulated. A similar method has also been suggested by Chapman, Murphy, Pounder and Purkis[229] who propose the use of ammonium persulfate, with or without sensitizing agents, such as sodium silicofluoride or trioxymethylene.

Deposition from Aggregated Latex. Although the deposition of latex on porous molds is ordinarily quite difficult, since the deposited material either clogs the pores or forms an impervious layer on the surface, deposition can be made comparatively simple by increasing the effective size of the particles. This increase can be accomplished by aggregation of the latex particles into relatively large groups. Agents which have been found to promote this aggregation include Irish Moss, phenol and trisodium phosphate, buffer solutions of phosphates, cinnamic and other aldehydes, and boric acid.[230]

Electrodeposition. The electrolytic deposition of rubber upon the anode is well known and is a subject which has been discussed considerably in the literature (p. 127 and p. 493 of this book, for instance). Several modifications of the normal electrodeposition process, which have been suggested recently, are of interest from the scientific point of view. These modifications consist of cathodic deposition, alternating current deposition, and internal current deposition. Cathodic deposition is made possible by changing the electrical charge on the latex particles. James and Twiss[231] have used such materials as acetic acid and formaldehyde in conjunction with protective colloids for this purpose, while the Siemens-Elektro-Osmose Gesellschaft[232] has employed thorium nitrate. Alternating current deposition is made possible by using two different materials, such as aluminum and carbon, for electrodes. In the case of internal current deposition, ammonium chloride is added to the latex in such a quantity that coagulation does not occur.[233] The electrodes used are made of carbon and of zinc. When the circuit is completed, a current flows through the cell, and rubber is deposited.

Gelling and Molding. Although the gelling of latex or compounded latex cannot alone be classed as a method of manufacture, it has been investigated as a preliminary step in the production of porous and other types of articles, not only by molding, but also by spreading, dipping, and spraying. The consistency of the latex is so changed by the gelling process that manufacture of the final article is often facilitated. Formaldehyde (alone or mixed with such substances as phenol and tannic acid), silicic acid, sodium silicofluoride, alum, magnesium sulfate, calcium chloride, saponin, gelatin, agar-agar, hemoglobin, other proteins and albumens, and cellulose xanthate are included among the substances which have been used as gelling agents.

Agents having little or no effect at room temperature, but a gelling or coagulating action at a somewhat higher temperature, are now coming into vogue.[234] Thus, although a small portion of certain substances, such as a salt of a bi- or a trivalent metal, will merely have a slight thickening effect on latex in the cold, it will cause further thickening and, finally, coagulation as the temperature is raised towards the boiling point. A preliminary gelling has been used to great advantage in the production of sponge rubber products in molds. In a process developed in England, a frothing agent, such as soap, and a gelling agent, such as sodium silicofluoride, are added to concentrated or thickened latex. After being beaten into a froth with a mechanical stirrer, the mixture is poured into a mold of the desired shape.[235] It is then gelled and vulcanized in the mold. Products made by this method are beginning to come into use for the upholstering of automobiles, furniture, etc.

According to a recent suggestion of Howard,[236] organic solvents may be added to latex as a preliminary step in the production of molded articles. The mass increases in volume during setting or vulcanizing and thus assumes the configuration of the mold. The solvent is claimed to function as a swelling or dissolving agent for the rubber, as a gas-forming agent, and as a gelling or setting agent.

Extruding. The production of articles, such as threads and tubes, by extruding the properly compounded latex into a coagulating or dehydrating bath, offers possibilities

[226] See Hadfield, U. S. Pat. 1,635,576 (1927) and Twiss, Brit. Pats. 285,938 and 297,911 (1928).
[227] See Anode Rubber Company, Brit. Pat. 291,805 (1928).
[228] U. S. Pats. 1,717,248 (1929) and 1,811,695 (1931).
[229] Brit. Pat. 326,782 (1930).
[230] See Hopkinson and Gibbons, U. S. Pats. 1,632,759 (1927) and 1,797,580 (1931); Smith, U. S. Pat. 1,678,022 (1928); Cadwell and Hazell, U. S. Pat. 1,802,753; Greenup, *Ind. Eng. Chem.*, **23**, 688 (1931).
[231] Brit. Pat. 334,581 (1930).
[232] French Pat. 669,275 (1930).
[233] See Williams, French Pat. 638,630 (1927).
[234] See Pestalozza, U. S. Pats. 1,717,248 (1929) and 1,811,695 (1931); Dunlop Rubber Company, Brit. Pats. 326,497; 326,782; 332,525; 332,526 and 333,952 (1930).
[235] See *Rubber Age* (*London*), **13**, 98 (1932).
[236] Brit. Pat. 381,975 (1933).

which do not seem to have been exploited until recently. According to a process patented by Murphy and Twiss,[237] compounded latex is allowed to flow by gravity through an orifice under the surface of a setting or dehydrating bath, which in a typical case may contain ammonium acetate and sodium chloride. The patent granted to Hopkinson and Gibbons[237a] has been used as the basis for the development of a commercial method for the production of rubber thread from latex.

Spraying. Although the spray process would appear to be particularly adaptable for the production of rubber coatings on objects which are of such intricate shapes or are in such inaccessible positions that other methods of coating cannot be used, the difficulties attending this method are such as to have limited its use thus far to a relatively narrow field. Clogging of the spraying devices, lack of smoothness in the dried film, and a tendency toward a lack of uniformity in the product are included among the difficulties. The translators have observed that sheets formed by the spray-drying of latex containing compounding ingredients are often striated. Although stocks containing a high proportion of pigments often exhibit a low tensile strength after being spray-dried and vulcanized, a brief period of milling of such stocks before vulcanization has been observed to increase the tensile strength considerably. The increase in properties is probably accounted for on the basis of the rupture of the individual rubber globules and a consequent improvement in the dispersion of the solid ingredients.

Impregnation of Fabric. One of the first uses suggested for latex was that of the impregnation of fabric. It has been shown by Dieterich[238] and by Hauser and Hünemörder[239] that the simple dipping of fabric in latex does not result in true impregnation. Nevertheless, Gibbons,[240] using the United States Rubber Company's flexing machine (see p. 586), has shown that from the standpoint of flexing life, latex-treated web fabric is far superior to cord fabric of the same construction. Various means for improving impregnation by pressure, vacuum, etc., have been tried. An interesting method for obtaining a coating of the individual fibers is that of Bongrand and Lejeune.[241] In this method, the latex is applied on the spinning frame while the fibers are in the roving stage.

A method for improving impregnation, which has been receiving an increasing amount of attention during the past few years, is that involving the use of latex to which a wetting agent has been added. These wetting agents, which are polar compounds, are adsorbed on the latex particles and prevent the latter from being adsorbed on the surface of the fabric. They influence markedly the interfacial tension between the fabric and latex. Sulfonated oils, sodium sulfanilate, thiourea, orthotoluidine, ammonium linolenate, saponin, and soluble salts of sulfonic acids, such as sodium isopropyl naphthalenesulfonate, are included among the agents which have been tried for this purpose. A report of a recent comparison of various wetting agents has been published by Hauser and Hünemörder.[242]

The Coagulation of Latex

Various Explanations of the Coagulation Process

General

Very different methods can be used for producing crude rubber from liquid latex. For example, a solid rubber can be obtained when the water contained in latex escapes by evaporating; naturally all the nonvolatile compounds present in the latex are found in this mass. Moreover, a more or less complete separation of rubber particles from the serum can be effected in many kinds of latex by centrifuging or filtration, and a rubber from which the greater part of the serum constituents has been separated is obtained. In most cases, however, the latex, by treatment with acetic acid, is transformed into a very white, gel-like mass from which commercial crude rubber is produced by pressing and drying.

[237] Brit. Pats. 311,844 (1929); 333,005 (1930); 326,496 (1930).
[237a] U. S. Pat. 1,545,257 (1930).
[238] *Ind. Eng. Chem., Anal. Ed.*, **2**, 102 (1930).
[239] *Metallges. Periodic Rev.*, **No. 5**, 31 (1931).
[240] *Ind. Eng. Chem., Anal. Ed.*, **2**, 99 (1930).
[241] Brit. Pat. 338,381 (1931).
[242] *Trans. Inst. Rubber Ind.*, **8**, 316 (1932).

The process by which latex is converted into a definite mass is usually designated as coagulation. Various authors have proposed the use of other terms but since none of these have been adopted in the literature, the present author prefers to retain the usual terminology.

The product formed by the coagulation of latex differs from a true gel (such as a gelatin swollen in water) in that a part of the liquid is much less strongly bound and can be made to flow out, as from a sponge, by a very light pressure. In such coagula the spongy structure of the network substance formed from the strong gel, is to be distinguished from the serum filling the meshes. The latter is readily separated by pressure (between rolls, for example), whereby the coagulum acquires a solid consistency.

Since the composition of the product varies with the coagulant used, the same latex can yield coagula in which the network structure and serum possess a very different chemical constitution. Variation in the coagulant can also lead to coagula in which the rubber particles are precipitated with different amounts of serum constituents, or with which the constitution of the adsorption hull is changed. In many coagulation processes, a part of the rubber particles may remain suspended in the serum, so that the latter exhibits a milky turbidity upon being pressed from the coagulum. In such cases, it appears correct to speak of an incomplete coagulation. In general, the network substance contains a certain amount of water (water of imbibition) which cannot be removed by pressure. This explains the observation (made by O. de Vries[243]) that the coagula contained about 3 to 10 per cent of water which cannot be separated by strong and long-continued pressure.

The exact investigation of the coagulation process has further shown that this process frequently precedes a more or less complete fusing of the rubber particles. Certain steps in the coagulation, for which various designations are customary, are to be distinguished. According to the terminology introduced by C. Beadle and H. P. Stevens,[244] it is suitable to distinguish between two stages of the coagulation process; namely, cream formation and floc formation.

In cream formation, the uniformly dispersed rubber particles separate from the serum and collect on the surface into a creamy mass. By shaking, a uniform dispersion is again obtained (reversible process).

In floc formation, a coalescence of the rubber particles to more or less large agglomerates takes place. These agglomerates tend to collect in the upper layer. By shaking, a uniform dispersion, but no disintegration of agglomerates, again takes place (irreversible process).

According to the coagulation process used, very different degrees of cream and floc formation can occur. It is possible in floc formation to observe all transitions between microscopically small agglomerates, consisting of only a few rubber particles, and large aggregates visible to the naked eye. Usually agglomerates of very different sizes are present in the same mass, and a coalescence of the flocs themselves takes place. In many coagulation processes an incomplete cream formation can take place, in which the serum remains clouded by rubber particles even on long standing, and only a part of the particles collect in the upper layer of the serum. The cream formation is also bound up with a more or less strong floc formation.

[243] de Vries, O., "Estate Rubber," p. 234. [244] *Kolloid-Z.*, 13, 217 (1913).

The incomplete coagulation process has been investigated[245] in the case of Hevea latex which was mixed with different amounts of aluminum sulfate. Upon the addition of small amounts of this salt, groups of rubber particles are formed which remain separated from one another at first and which show only a slight motion, mostly longitudinal vibration. The addition of greater quantities of aluminum sulfate results in the formation of larger groups of rubber particles, which are always more crowded together and appreciably deformed. They finally flow together and unite so intimately that the individual rubber particles are no longer to be distinguished. Whether a bursting of the rubber particles takes place could not be determined in the experiments.

True coagulation is by no means always preceded by visible cream and floc formation. In the case of the latex of *Manihot Glaziovii,* for example, the addition of sufficient acid immediately results in the formation of a coherent mass of the same volume as the latex.

If an insight into the chemical-physical and colloid-chemical changes taking place during the coagulation is to be obtained, consideration must be given to the fact that latices from the various species of rubber plants possess very different kinds of structures and can exhibit very different behaviors when similar coagulating processes are used. It is therefore not permissible to generalize and attempt to derive a generally applicable explanation of the coagulation phenomenon from observations made on latex from one or a few species, or results obtained with but a single coagulant. On the basis of the investigations thus far reported, the author thinks it probable that the processes involved in the coagulation of latices are not always the same, and that at this time no generally satisfactory explanation may be given for many of them. A critical discussion of the various explanations of coagulation and of the observations upon which these explanations were based will be presented later.

Size of the Rubber Particles

The size of the rubber particles is of significance in cream formation, which precedes actual coagulation in many coagulation processes. It was shown by E. Fickendey[246] and D. Spence[247] that those latices which cream most rapidly and most completely contain the largest particles. It was further observed by V. Henri[248] that in a high column of diluted Hevea latex, the largest particles collect nearest the upper surface. The size of the rubber particles is of particular significance in coagulation processes depending on centrifugal force. For example, the especially large rubber particles contained in Castilloa latex are very readily separated from the serum, while fresh Hevea latex cannot be completely creamed by centrifuging. On the other hand, the size of the rubber particles is entirely without significance in coagulation processes depending upon the addition of chemical reagents.

Brownian Movement

Brownian movement tends to promote the uniform distribution of the rubber particles in latex. Since the intensity of this motion decreases with the size of the rubber particles, it is apparent that a latex which

[245] See *India Rubber World,* **68,** 706 (1923).
[246] *Tropenpflanzer,* **14,** 481 (1910).
[247] *Kolloid-Z.,* **4,** 204 (1909).
[248] See "Lectures on India Rubber," edited by D. Spence, p. 206, **1909.**

contains many large rubber particles is less stable and tends to cream more than one with smaller rubber particles. To what extent Brownian motion plays a role in floc formation and creaming has not yet been ascertained with certainty. It was shown by E. Fickendey[249] that the coagulation of latex by heating could be explained by the increase in amplitude of vibration and the thereby increased probability of collision of the rubber particles. It is to be considered that, on heating, various processes which are of influence upon the result of the coagulation also take place in the serum.

V. Henri[250] found that the intensity of the Brownian movement is quickly decreased and finally entirely stopped before coagulation begins in case of the addition of coagulants, such as acids. Even upon the addition of alkalies, which do not cause coagulation, the intensity of the motion is considerably reduced. It was stated by C. Beadle and H. P. Stevens[251] that the Brownian motion comes to a standstill without the occurrence of coagulation when sufficient acid is added to the latex so that the concentration is just below that necessary for complete coagulation.

Increase of the Tackiness of the Rubber Particles

Aggregation or coagulation is traced back by some authors to the greater tackiness which the rubber particles acquire under certain conditions. A. W. de Jong and W. R. Tromp de Haas,[252] on the basis of investigations carried out with Castilloa latex, in which acetic acid, alcohol and acetone served as coagulants, have explained the coagulation process as follows: The surfaces of the rubber particles are so changed by the dissolving of the resin by the reagents that a greater adhesiveness is obtained, and therefore, when the particles collide, they immediately adhere to one another. In refutation of this assumption, it was shown by C. O. Weber[253] and others that the resin is not at all soluble in acetic acid and that the rubber is more tacky the richer it is in resin. As with acetic acid, a solution of the resin cannot be obtained with most of the other coagulants used.

A. W. K. de Jong and W. R. Tromp de Haas[254] also assumed that the tackiness of the rubber particles is increased by heating, and that coagulation is thereby effected, especially with purified Castilloa latex. E. Fickendey[255] is of the opinion that the coagulation of protein-free latices is promoted by boiling, because the rubber particles become more tacky and consequently adhere more strongly to each other when they come in contact. To what extent this explanation is correct cannot yet be judged. It is known, however, that rubber particles (or aggregates of the same) collected on a filter can be bound together by a very light pressure.

Influence of the Specific Gravity of the Serum on the Creaming of Latex

The specific gravity of serum can play a certain role in cream formation. It is relatively great in a latex which creams very readily (such as Castilloa latex). According to C. Beadle and H. P. Stevens,[256] the value

[249] *Kolloid-Z.*, **8**, 45 (1911).
[250] See "Lectures on India Rubber," edited by D. Spence, p. 204, **1909**.
[251] *Kolloid-Z.*, **13**, 207 (1913).
[252] *Ber.*, **37**, 3301 (1904).
[253] *Gummi-Ztg.*, **19**, 101 (1904).
[254] *Ber.*, **37**, 3301 (1904).
[255] *Kolloid-Z.*, **8**, 45 (1911).
[256] *Kolloid-Z.*, **13**, 210 (1913).

for the specific gravity is considerably over 1.0 in Castilloa latex of 40 per cent rubber content. The specific gravity of the serum cannot entirely explain cream formation. In the case of the latices of many species (such as *Manihot* and *Kickxia*) the tendency to cream is increased by the addition of pure water, which must cause a decrease in the specific gravity of the serum. It appears still less probable that a change in specific gravity caused by the addition of coagulants will play a role in creaming, as was assumed by A. W. K. de Jong and W. R. Tromp de Haas[257] and J. H. Hart.[258] Evidence against this assumption is furnished by the fact that most coagulants function in such small amounts that the specific gravity of the serum is changed only a little by their addition.

Role of the Proteins

The proteins contained in latex play an important role in many coagulation processes, such as the normal coagulation of Hevea latex with acetic acid. Evidence for this statement is provided by the facts that (as was established by H. Freundlich and E. Hauser[259]) the limits of the hydrogen-ion concentration in which coagulation of Hevea latex takes place correspond with the coagulation limits for proteins, and that, according to E. Hauser,[260] the protein-rich serum obtained by filtration through a ceramic filter also precipitates at the same hydrogen-ion concentration.

It was further established by P. Scholz[261] that Hevea latex is also coagulated by the addition of proportionately smaller amounts of other typical protein coagulants (copper sulfate, aluminum sulfate and lanthanum nitrate). The required quantities of such agents were smaller the more the latex was diluted before the addition of the coagulant. In latex freed as completely as possible from proteins, dilution exerts no marked influence on the ease of coagulation.

Since a considerable portion of the proteins goes into the network structure of the coagulum upon coagulation with acid, the presence of the 3 per cent or so of proteins found by analysis in rolled and washed sheet or crepe rubber is understandable. A part of the proteins contained in the latex remains in the serum. In fact, as was established by N. Beumée-Nieuwland and O. de Vries,[262] proteins which are precipitated by warming are also found in the serum.

It is assumed by many authors that the protein shells surrounding the rubber particles fuse together during coagulation. According to the observations of C. Beadle and H. P. Stevens,[263] the rubber particles of Hevea coalesce to form an irregularly shaped fibrous network, on the edges of which the outlines of the single particles are preserved.

In most methods of coagulation of latices of other plants large amounts of proteins are precipitated. Furthermore proteins are at least partly coagulated by the coagulants commonly used, as well as by heating.

Kickxia latex, which, as was established by E. Fickendey,[264] probably contains peptones instead of proteins, and is coagulated not by protein coagulants but by peptone coagulants, is of special interest in this respect.

[257] *Ber.*, **37**, 3305 (1904).
[258] *Rev. cult. coloniales*, **8**, 81 (1901).
Kolloid-Z., **36**, (Supplementary Volume), 24 (1925).
Hauser, E., "Latex," p. 96, Th. Steinkopff, Dresden and Leipzig, **1927**.
[261] *Kautschuk*, **4**, 5 (1928).
[262] *Arch. Rubbercultuur*, **11**, 527 (1927).
[263] *Kolloid-Z.*, **13**, 207 (1913)
[264] *Kolloid-Z.*, **8**, 43 (1911).

There is no doubt that an aggregation of rubber can be brought about without the help of proteins. A. W. K. de Jong and W. R. Tromp de Haas[265] found that Castilloa latex coagulated with alcohol was free from proteins, and that latex from the same plant, freed of all proteins by twelve washings, coagulated just as well as non-washed, protein-containing latex. H. C. Gardner[266] proved that Hevea, Castilloa and Micrandra latices, after digestion of the protein with papain and separation of the digested albumin by dialysis, aggregated upon the addition of alcohol. G. S. Whitby[267] obtained a nitrogen-free rubber by treating Hevea latex with a neutral solution of sodium sulfate at 70° C. Floc formation occurred immediately, and on the following morning the rubber separated from the serum as a coherent mass (in which proteins were not to be found).

It has already been shown by various authors that latices freed from proteins behave differently from fresh latex. It was observed by H. Freundlich and E. Hauser[268] that the residue of Hevea latex remaining on the filter after filtering off the serum gives a colloidal solution with water, for even a partial coagulation of which larger amounts of acid are necessary. By repeated filtration, it is possible to obtain a product which can no longer be coagulated by acids or other known coagulants.

According to E. Hauser,[269] Hevea latex in which the protein is digested with trypsin shows properties different from those of fresh latex. In this "trypsin" latex the formation of a single clump occurs simply upon shaking, while in fresh latex a flocculation takes place, and a milky liquid may be again obtained by vigorous agitation.

It appears correct to distinguish between the various steps in coagulation, as was probably first done by C. O. Weber.[270] He designated the aggregation of the particles occurring without help of proteins as coalescence, in contrast to true coagulation which occurs with the assistance of proteins. The designation "agglutination" is used by other authors for the first-mentioned process. The principal difference between true coagulation and agglutination is that in the former an aggregation of the particles is caused by coagulation of the proteins, while in agglutination it is caused by a direct fusing of the rubber particles. Which of these processes is effective cannot yet be determined with certainty in the cases of many methods of coagulation. Likewise it cannot be stated with certainty which of these processes yields the best rubber. It can be considered as very probable that the protein content of crude rubber exerts a favorable influence upon its behavior during vulcanization and on the physical properties of the resulting vulcanizate, especially after aging.

A completely different opinion regarding the action of the proteins was expressed by E. Fickendey.[271] According to his opinion, the proteins act as protective colloids in the latex of the living plant, and the coagulation is caused by the loss of the protective power of the proteins. Fickendey based his opinion on observations made on Kickxia latex. He found that in this latex creaming and coagulation are effected by dilu-

[265] *Ber.*, **37**, 3301 (1904).

[266] International Rubber and Allied Trades Exhibition, Ltd., London, **1911**.

[267] *Kolloid-Z.*, **12**, 147 (1913).

[268] *Kolloid-Z.*, **36** (Supplementary volume), 20

E., "Latex," p. 97
Dresden and Leipzig, **1927**.

[270] Weber, C. O., "Reise nach einer Kautschukplantage in Columbien," Dresden, **1903**.

[271] *Kolloid-Z.*, **8**, 43 (1911).

tion with water. This phenomenon was traced to the fact that the peptones contained in the latex had lost their effectiveness through dilution. If too much flocculation has not taken place during creaming, the rubber particles may again be uniformly dispersed by shaking, and by the addition of pure serum or a 4 to 8 per cent solution of peptone. The suspension thus again obtained has the same stability as fresh, undiluted latex. Fickendey was also able to obtain a reasonably stable suspension by shaking the cream from Castilloa latex with a 10 to 15 per cent protein solution.

A. W. K. de Jong[272] had previously made a similar observation to the effect that washed, purified Castilloa latex was converted by the addition of some egg-white to a latex which showed exactly the same properties as latex collected from the tree. The observed prevention of the coagulation was explained by de Jong in an entirely different manner, however.

E. Fickendey was able to obtain agglutination in Kickxia latex by dialysis. He explained this result on the basis of the removal of the peptones. How applicable Fickendey's explanation is to other coagulation processes is still to be investigated. It does not appear to hold for the latex of *Manihot Glaziovii*. The present author[273] has previously observed that the latex of this plant, although especially rich in proteins, coagulated very readily after slight dilution with water, even without the addition of coagulants. On the other hand, if it is diluted with very much water (about 100 volumes) coagulation no longer takes place, even after a long time, especially when a disinfectant is added. Recently P. Scholz[274] concluded from experiments in which fresh and practically protein-free latex was precipitated that the rubber particles in latex are protected by proteins against coagulation by univalent electrolytes but sensitized to coagulation by divalent ones.

Role of the Resins

Since resins and resin acids are precipitated only by a much higher hydrogen-ion concentration ($pH = 2$) than is necessary for the coagulation of latex, while the sodium salts of resin acids are precipitated by a lower hydrogen-ion concentration ($pH = 6$) and therefore cannot be contained in fresh latex, it follows, as was established by H. Freundlich and E. Hauser,[275] that resin compounds can play no role in the coagulation of latex by acetic acid.

According to the investigation of O. de Vries and N. Beumée-Nieuwland,[276] the dissolving of resins (which might have been functioning as protective colloids) can play no role in the coagulation of latex with alcohol, since the concentration of alcohol present in the case of complete coagulation is much too small to dissolve the resins. The rubber obtained by coagulation with alcohol shows no smaller acetone-soluble content than that obtained by coagulation with acetic acid.

Influence of the Substances Dissolved in the Serum

It was demonstrated by the experiments of C. Beadle and H. P. Stevens[277] and of P. Dekker,[278] all of whom worked exclusively with

[272] *Ber.*, **37**, 4398 (1904).
[273] Zimmerman, A., "Der Manihot-Kautschuk," p. 161, G. Fischer, Jena, **1913**.
[274] *Kautschuk*, **4**, 5 (1928).
[275] *Kolloid-Z.*, **36** (Sup. vol.), 19 (1925).
[276] *Arch. Rubbercultuur*, **11**, 498 (1927).
[277] *Kolloid-Z.*, **13**, 211 (1913).
[278] *Delft. Comm.* **1**, 24.

ammonia-preserved latex, that the material contained in latex serum is not without influence on the coagulation process. Beadle and Stevens found that preserved latex, after it had been dialyzed two or three days with water, could be coagulated upon the addition of acetic acid. Upon allowing such latex to stand a few days flocculation occurred, however, and it was no longer possible to cause coagulation with acetic acid. Dekker observed that dialyzed latex is difficult to coagulate with acetic acid or by heating, but that coagulation again takes place upon addition of the dialysate.

Role of Microörganisms and Enzymes

Spontaneous coagulation of Hevea latex is attributed by various authors to the action of microörganisms and enzymes. This coagulation takes place when latex stands quietly in air and is usually finished within 24 hours. It is sometimes incomplete, however, so that upon squeezing the coagulum a more or less milky serum flows out. Various processes take place in spontaneous coagulation. To what extent these processes are connected with the actual coagulation cannot yet be determined with certainty. When the ordinary coagulation or the drying of the coagulum proceeds slowly, similar processes also take place. Maturation is the term applied to these processes.

Two of the phenomena to be discussed take place on the surface of the latex, or of the coagulum; namely, slime formation, and the appearance of a violet color. Decomposition processes, especially those resulting in the formation of acids, occur on the inside. These three processes are to be considered somewhat more in detail, although the consideration is to be limited to the most important observations. In reference to the older literature the compilation of O. de Vries[279] must be consulted.

Slime Formation. The slimy mass formed on the surface in contact with air shows a more or less strongly alkaline reaction and a yellowish color. It usually contains flocs of rubber which are lost in the washing of the coagulum, and also various decomposition products, among which are foul-smelling decomposition products of the proteins. Slime formation does not occur in the absence of air.

The origin of the slime is usually attributed to aerobic bacteria. G. Vernet[280] was able to isolate a motile bacillus from the slime.

Darkening. Darkening of the surface of latex and of the coagulum is primarily due to oxidizing enzymes (oxidase, peroxidase, or tyrosinase) by means of which the melanin-like substances are produced in latex. Since this process takes place in the serum, O. de Vries[281] was able to observe a darkening of serum separated from the coagulum.

Very marked darkening (dark violet to blue-black) can frequently be observed on the surface of dried latex strips (scraps) on the outer surface of the bark of the tree. Individual trees behave differently in this respect, and usually the color of scraps from young parts of the bark is darker than that of scraps from old bark. These different behaviors can be traced to the fact that, in the latex concerned, the oxidizing enzyme or the oxidizable substance is present in different amounts, or one of them is entirely missing. An experiment of A. W. K. de Jong,[282] in which latex which did not show darkening directly showed it after ad-

[279] de Vries, O., "Estate Rubber," p. 159, 200, 242.
[280] *Bull. Marseille*, 1, 118 (1919).
[281] de Vries, O., "Estate Rubber," p. 30.
[282] *Mededeel. Agr. Chem. Buitenzorg*, No. 10 (1915).

dition of tyrosin, speaks for the lack of oxidizable substance. The fact that darkening does not occur in the case of a coagulum obtained from latex which has been previously warmed is attributed to destruction of the enzymes. Any microörganisms present could also be destroyed by such means.

Darkening can be prevented by the exclusion of air from the coagulum or the addition of an antioxidant. Sodium acid sulfite ($NaHSO_3$), by means of which the catalytic oxidation is prevented, is usually employed in practice for this purpose.

Whether the oxidizing enzymes are or are not already present in the laticiferous elements of the living plant is not yet definitely known. The absence of enzymatic action, in spite of the presence of enzymes, can have its basis in the fact that the enzymes in the living latex elements are separated from the oxidizable material. Moreover, the oxygen necessary for activation of the enzymes may not be present in a sufficient amount in the latex of the living plant. Furthermore, it is quite possible that the enzymes contained in latex do not even come from the latex vessels, but from the cells of the bark parenchyma which are cut at the same time the laticiferous elements are tapped. The fact that G. Vernet [283] detected peroxydase in parenchyma cells surrounding the latex vessels gives evidence for this assumption. That the enzymes in the latex collected after tapping may have been first produced by bacterial action is a further possibility.

Decomposition Phenomena. A continuously increasing formation of acid takes place in the inside of the latex and of the coagula from which oxygen is entirely excluded. As was established by K. Gorter and N. L. Swart,[284] lactic acid, small amounts of acetic acid, and traces of succinic acid are found therein. The material for this acid formation is probably supplied chiefly by the carbohydrates in the latex. The fact that (as found by O. de Vries [285]) acid formation can be accelerated by the addition of sugar confirms this conjecture. D. Spence [286] offered the view that the acid formation occurring in spontaneous coagulation is brought about by enzymatic cleavage of protein compounds having a complex carbohydrate structure.

Simultaneously with acid formation, gas bubbles, which cause a spongy appearance, separate in the coagulum. According to O. de Vries,[287] the gas bubbles, in the beginning of the decomposition, contain about 50 per cent of carbon dioxide. Some combustible gas (methane or hydrogen?) and some incombustible gas (nitrogen?) are also contained therein. In the course of time, the amount of combustible gas decreases and the carbon dioxide increases, until finally the latter can amount to more than 95 per cent.

In the later stages of spontaneous coagulation, decomposition of the proteins, with formation of hydrogen sulfide, amino acids, and amines, takes place. Probably the accelerator of coagulation functioning in the case of spontaneous coagulation is to be found among these decomposition products.

The decomposition processes described are usually attributed to the action of anerobic bacteria. Two species of bacteria, one of which changed the sugars in latex into acids, and the other of which decomposed or liquefied the protein matter, were isolated from latex by A. Denier and G. Vernet.[288] Whether these bacteria have such a universal distribution that they are to be found in every sample of latex which stands in the air, or whether other

[283] *Bull. Marseille*, 1, 111 (1919).
[284] *Mededeel. Rubberproefsta. West Java*, No. 6.
[285] de Vries, O., "Estate Rubber," p. 207.
[286] "Lectures on India Rubber," p. 198, 1909.
[287] de Vries, O., "Estate Rubber," p. 238.
[288] *Compt. rend.*, 165, 123 (1917).

species of bacteria can assist them, may be definitely established only by careful infection experiments with completely sterilized latex.

Spontaneous Coagulation. Spontaneous coagulation is attributed entirely to the action of enzymes by some workers, and to decomposition processes caused by anerobic bacteria by others.* A safe conclusion to this debated question will only be reached when it is possible to sterilize latex without decomposing the enzymes, and to make the enzymes inactive without destroying the bacteria present. It appears impossible as yet to fulfill either of these requirements.

The enzyme functioning in the case of spontaneous coagulation is usually designated as protease or coagulase. It is thereby implied that this enzyme acts especially on the protein contained in the latex.

In favor of the enzymatic action, it was adduced by G. S. Whitby [289] that spontaneous coagulation will commence much more quickly than decomposition processes ordinarily begin and that the odor of the latex, when it has set to a solid mass, will still be quite fresh. In this connection it is nevertheless to be observed that acid formation begins in the latex immediately after the latter flows out of the wound, according to concordant statements of different workers, and that protein decomposition, evolving foul-smelling material, can be an entirely independent process.

W. Barrowcliff [290] has shown that bactericides such as toluol and thymol, which are not in general effective with enzymes, do not prevent spontaneous coagulation, while hydrocyanic acid, on the contrary, makes the enzymes inactive and prevents spontaneous coagulation. The observations on latex sterilized by the Barrowcliff method (pouring fresh latex, with constant stirring, into an equal volume of water heated to 90° C.) furnish evidence in support of the enzyme theory. This latex (latex "B") remains unchanged for days in open vessels. It is quickly coagulated, however, when it is "inoculated" by adding a drop of fresh latex. The assumption is that the coalase in latex "B" has been rendered inactive by the heating, but that by the addition of fresh latex a sufficient amount of coalase is added to bring about coagulation. It is apparent that in this case, coagulation is a question of enzymatic action, since even an exceedingly small amount of fresh latex is sufficient for coagulation. According to O. de Vries and N. Beumée-Nieuwland,[291] four drops of fresh latex have the same coagulating action as 15 cc. of alcohol or 121 mg. of alum. From the dried coagulum obtained from latex "B" through inoculation, these same authors [292] were also able to obtain with dilute sodium carbonate solution an extract which still exhibited an inoculating action on latex "B." Furthermore, an extract which showed distinct inoculating action could be obtained once more from the coagulum obtained by using the previously mentioned extract. This extraction process did not succeed the third time, however.

Since the serum pressed from a coagulum obtained by normal coagulation with acetic acid causes no coagulation, it is to be assumed that the coalase is completely precipitated by the acetic acid. In fact, by extracting the acetic acid coagulum with a dilute soda solution, it was possible to obtain an extract suitable for inoculation.

* Translator's Note. During a bacteriological study of Hevea latex, A. S. Corbet [*Rubber Res. Inst. Malaya, Bull.* No. 1 (1929)] found that one organism predominates. He proposed the name of *Bacillus pandora* for this organism. *B. pandora* is capable of decomposing latex substances to produce acids, and thus bring about separation of the rubber particles. V.N.M.

[289] *Kolloid-Z.*, 12, 151 (1913).

[290] *J. Soc. Chem. Ind.*, 37, 48T (1918).

[291] *Arch. Rubbercultuur*, 11, 503 (1927).

[292] *Arch. Rubbercultuur*, 11, 530 (1927).

It is doubtful whether all the phenomena described can be attributed to bacterial action alone. In view of the great heat resistance of many bacteria, it cannot be accepted as proved that all the bacteria in latex "B" are killed by the Barrowcliff method of sterilization. If it is assumed that all the bacteria are killed in latex "B," an explanation is still to be provided for the fact that this latex remains sterile in the air whereas fresh latex is usually quickly precipitated by bacteria. A possible explanation is that the coagulating bacteria in latex "B" fail to obtain sufficient food for their development. It is known that the protein in the latex undergoes a change upon heating. It was stated by E. Hauser [293] that latex "B" coagulates in a short time after the addition of pure casein solution. Whether this coagulation is brought about as a consequence of the renewal of the process of acid formation by bacteria is a question yet to be answered. That the results of this experiment may be brought in some manner into agreement with the enzyme theory is a further possibility.

Action of Electrolytes

The relation between electrical processes and various coagulation phenomena, especially acid coagulation of Hevea latex, have been considered by numerous authors.

Upon the addition of acids to Hevea latex, coagulation begins [294] as soon as the pH value sinks to about 4.8, and occurs rapidly at a pH of 4.5. If the pH sinks lower, however, coagulation is again retarded, and at a pH of 3 the latex can remain liquid for several days. Coagulation again occurs upon further addition of acid. Latex, which, upon the addition of large amounts of acid, does not coagulate, is designated as latex of the second liquid zone, and the coagulation taking place upon a still greater addition of acid is designated as coagulation of the second zone. It was established by V. Henri [295] that the rubber particles move to the anode upon the passage of an electrical current through Hevea latex. The particles are therefore negatively charged. According to W. N. C. Belgrave,[296] a reversal of the charge on the rubber particles occurs in the second liquid zone.

R. G. Fullerton* [*Quart. J. Rubber Research Inst. Malaya,* **2,** 158 (1930)] has recently studied the effect of hydrogen ion concentration on the coagulation of fresh, of preserved, and of centrifuged latex, using the quinhydrone electrode. It was observed that with fresh latex of from 4 to 35 per cent rubber content the range of pH values defining the transitional stage between the first liquid zone and the zone of complete coagulation increased as the rubber content of the latex increased. On the other hand the range of values defining the condition of flocculation decreased as the rubber content increased until a rubber content of 15 per cent was reached, at which point this stage disappeared. It was found that there was no second zone of complete dispersion with latices of 20 to 35 per cent rubber content. With latices of greater dilution dispersion was complete in the second zone (pH 3.5 to 1.0). Latex preserved with ammonia behaved in the same way as fresh latex, but latex preserved with formalin and diluted to 10 per cent rubber content would not coagulate at any pH lower than 7.0. Latex preserved with sodium hydroxide coagulated normally in the two zones of coagulation but had no second liquid zone. Centrifuged latex behaved in the same manner as did latex preserved with sodium hydroxide.

[293] Hauser, E., "Latex," p. 95, Th. Steinkopff, Dresden and Leipzig, **1927.**

[294] *Cf.* G. S. Whitby, *Kolloid-Z.*, **12,** 156 (1913); H. Freundlich and E. Hauser, *Kolloid-Z.*, **36,** (Supplementary volume), 18 (1925); O. de Vries and N. Beumée-Nieuwland, *Arch. Rubbercultuur,* **10,** 503 (1926).

[295] *Compt. rend.*, **144,** 431 (1907) and "Lectures on India Rubber," edited by D. Spence, p. 203, **1909.**

[296] *Malayan Agr. J.*, **11,** 348 (1923).

* Translator's note by H. W. G.

In the acid coagulation of Hevea latex, the question is one of a so-called "irregular" series, such as has also been observed in the case of the agglutinating bacteria. Hauser concluded, from the similar behavior of these bacteria and the rubber particles, that the latter are also surrounded by an adsorption hull of protein. It may be assumed with great probability that this adsorption hull plays a large role in coagulation with acids, as was mentioned on page 98. The investigations thus far conducted do not permit the making of any positive deductions regarding the changes taking place in this hull upon the addition of acids. Evidently a part of the materials dissolved in the serum (such as the proteins, which may exert an influence on the consistency of the coagulum) are also precipitated upon the addition of acids.

The acid added for coagulation is not entirely chemically combined, but is partly adsorbed.[297] It is difficult to remove the adsorbed part from the coagulum by washing or dialysis.

Hydration

Ordinarily it is not easy to judge by experiments with dehydrating electrolytes whether the changes produced by them in latex are to be traced to a change in hydration or to ionic action. Dehydration is probably the factor involved when (as observed by O. de Vries and N. Beumée-Nieuwland[298]) pieces of potassium and sodium hydroxide are placed in undiluted latex and immediately become covered with a thick layer of coagulated rubber.

Likewise, changes in hydration are probably of primary importance in coagulation caused by alcohol. Whether it is the proteins or the rubber itself which becomes dehydrated remains a question. O. de Vries and N. Beumée-Nieuwland offered the view that a change in hydration of the rubber particles is the major consideration. In support of this view they cite the facts that the rubber obtained by coagulation with alcohol is not distinguished by an especially high nitrogen content, and also that latex almost completely freed of nitrogen-containing material is coagulated in the same way as fresh latex. These authors did not express an opinion regarding the mechanism involved in this change in hydration.

Separation of Serum from the Coagulum

It has been observed by various workers that serum separates from the coagulum before, during, and after rolling. In the following section, an explanation of this observation is sought on the basis of the assumption that the fresh coagulum consists of a network structure of rubber particles with serum filling the meshes of the network. (*See* p. 95.) The coagula have structures like those of bath sponges but differ from the latter by having greater fineness of pores and also by the fact that their "girders," when they come in contact, fuse together and thus bring about a considerable decrease in capillary space, but an increase in the strength of the network. The framework substance can contain water (water of imbibition) in various amounts. This water can escape from the structure particularly by transpiration.

The case in which a pressure is exerted on a small strip of coagulum, for example a sheet passing through the rolls, is first to be considered. It is manifest that the serum is pressed into the capillary spaces of the adjacent

[297] See W. Crossley, *India Rubber J.*, **18**, 11 (1911).
[298] *Arch. Rubbercultuur*, **11**, 497 (1927).

parts of the sheet, whereby an increase in capillary spaces contained in them is produced and a considerable stretching of the rubber network results. Consequently, serum must flow from both sides of the strip on both sides of the compression zone. In fact, the amount of serum flowing from the unrolled part is greater than from the part already rolled, since shrinkage of the capillary space is involved in the rolling.

Since the sheet after pressing has a fixed thickness, it is conceivable that the flow in the capillary spaces (which set up a greater or smaller resistance to the movement of the serum, according to their width) requires a certain amount of time and that the complete release from stretch of the inner part of the rubber network takes place only after a longer time.

Such a long-continuing separation of serum from sheets of Manihot Glaziovii was observed by the author.[299] This could also be observed when the sheets were placed under water after rolling. If the sheets were dipped in hot water for a few minutes, a pronounced separation of serum immediately took place. This apparently is to be traced to the "girders" of the rubber structure contracting until the rubber was completely solidified.

Similar observations were made by O. de Vries [300] on wet sheets of Hevea rubber. He observed that liquid was absorbed when such sheets were stretched and an increase in capillary space evidently thereby produced. As soon as the tension of the sheet was released and the meshes were again contracted the liquid was given off once more. The further observation of de Vries that upon bending a freshly prepared sheet serum flows out only on the concave side, and that this serum is again absorbed when the sheet is bent in the opposite direction may be explained in the same manner.

A further flow of serum from sheets hanging in the air can occur, since the outer layers contract through loss of water and exert a pressure on the inside. This behavior is even more striking in the case of wet balls of rubber. The author,[301] for example, has observed a pronounced spontaneous separation of serum from balls of Manihot Glaziovii obtained by the Lewa method. The previously mentioned "sweating" of the large balls of Para rubber may be explained in this manner.

According to O. de Vries,[302] it is possible for the coagula from diluted latex to contract with loss of serum, even when no pressure is exerted on them, and also when they are dipped entirely under water so that evaporation is prevented. The explanation of this observation is that chemical changes, which lead to compression of the rubber, are taking place in the rubber network. In fact, it was observed that the sheets gradually became more solid while immersed. The fact that such a contraction does not take place in the coagulum from undiluted latex depends upon the fact that the rubber network possesses such strength to begin with that upon maturation no further structure changes take place.

The structure of the rubber network appears to be of significance for the drying of rubber, which depends upon transpiration. It is known that crepe rubber dries more quickly than sheets of the same thickness. This is attributed largely to the fact that a porous structure is acquired through the continued rupture and re-uniting of the rubber network in the preparation of the former.

[299] *Pflanzer*, **8**, 389 (1912).
[300] de Vries, O., "Estate Rubber," p. 233.
[301] *Pflanzer*, **8**, 394 (1912).
[302] de Vries, O., "Estate Rubber," p. 231.

The Origin of the Nerve [303] of Crude Rubber

Coagula made from the same latex usually possess greater nerve the less water they contain. A rubber coagulum made from Hevea latex by coagulation with acetic acid is a white, scarcely elastic, and easily ruptured mass. Upon pressing the coagulum between rolls, however, it can be observed that the nerve of the sheet increases immediately. A further, usually very marked increase in nerve takes place upon complete drying of the sheet. It can be assumed on the one hand that with the loss of water the fibers in the rubber network contained in the rubber "curd" come more and more together and fuse, and on the other hand that the fibers themselves steadily become stronger through loss of their water of imbibition. However, the rubber particles themselves and the foreign substances contained in the rubber network may play a role. Still, it is worthy of note that rubber from which almost all foreign substances, especially nitrogen-containing compounds, have been removed as completely as possible in its preparation can possess nerve to a pronounced degree.

The nerve of crude rubber is largely dependent upon the method of preparation used in all cases. It is known that crepe rubber, in the manufacture of which a continuous rupture of the rubber takes place, possesses a correspondingly small nerve. In contrast, rubber in the manufacture of which the latex or the still wet coagulum is heated, is usually distinguished by great nerve. Crepe rubber acquires greater nerve if, after drying, it is heated and pressed. To explain such a process, F. Kirchhof [304] assumes that through the mechanical working of the rubber the hulls surrounding the individual rubber particles are ruptured so that a fusion of the inner parts of the particles can take place. In fact, it has been stated [305] that rubber particles lose their original shape and burst upon drying. However, this assumption does not explain, among other things, the fact that the cream collected on the filter from flocculated rubber particles can be united with a light pressure of the fingers to form rubber which exhibits good nerve when dried.

The view was expressed by C. O. Weber [306] that in the development of nerve in rubber a polymerization of the rubber molecules takes place. He based this view on the fact that strengthening of the coagulum during rolling takes place rather suddenly, and that the hydrocarbon in latex, in contrast to that in crude rubber, is insoluble in ether. The correctness of the latter statement has been disputed by various workers, such as R. Ditmar,[307] A. W. K. de Jong and W. R. Tromp de Haas,[308] C. Harries,[309] W. Esch and A. Chwolles,[310] and others. Harries [311] emphasized that by treating fresh latex with ether a colloidal solution is immediately obtained, from which it follows that the molecule of this substance is fairly large and cannot be a diterpene, $C_{20}H_{32}$.

According to E. Fickendey [312] no change in volume and no increase in temperature takes place upon conversion of liquid rubber into tough, elastic rubber.

[303] The term "nerve" as applied to rubber carries with it the conception of toughness accompanied by elasticity.
[304] *Kolloid-Z.*, **35**, 367 (1924).
[305] *India Rubber World*, **68**, 706 (1923).
[306] *Ber.*, **36**, 3108 (1903).
[307] *Chem. Ztg.*, **29**, 175 (1905).
[308] *Ber.*, **37**, 3301 (1904).
[309] *Ber.*, **38**, 1195 (1905), and *Gummi-Ztg.*, **24**, 850 (1910).
[310] *Gummi-Ztg.*, **19**, 165 (1904).
[311] *Gummi-Ztg.*, **24**, 851 (1910).
[312] *Kolloid-Z.*, **8**, 46 (1911).

Methods of Converting Latex into Crude Rubber

HEVEA

The Brazilian Smoking Method

In the virgin forests of Brazil the smoking process for the coagulation of Hevea latex has been used without variation for a very long time. According to Labroy and Cayla,[313] the smoke used is obtained by burning such materials as wood rich in resin (species of *Silvia, Mimusops, Tecoma* and others), the fruits (nuts) of the palms *(Attalea excelsa, "urucuri," Maximiliana regia, Astrocaryum Tucuma, Orbignya speciosa)*, or the shells of Brazil nuts *(Bertholletia excelsa)*. By making use of a funnel-shaped flue the fire is so regulated that the smoke leaves in the form of a thick cone. (Fig. 36)

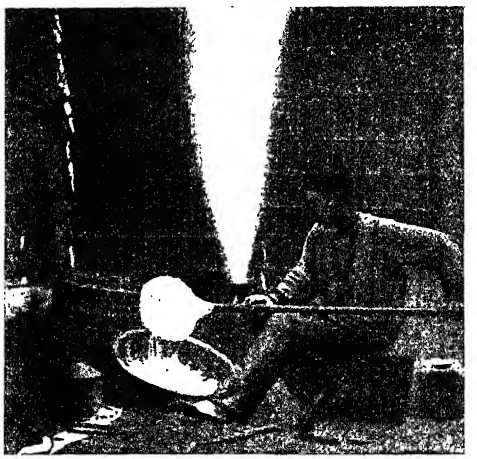


Figure 36—Smoking of latex in the Amazon territory.

(Courtesy of H. Schüler.)

In order to bring the latex into the smoke, the native uses a spade-shaped instrument, consisting of a wooden disc fastened to a long handle. This instrument, after being covered with a layer of latex by a pouring or dipping process, is rotated in the cone of smoke until the latex is entirely coagulated and sufficiently dried. This disc is then covered with another layer of latex and the smoking repeated. This process is continued until all of the latex collected that particular day has been coagulated. The ball of rubber obtained is enlarged by a continuation of the process on succeeding days, usually until it has attained a weight varying from 10 to 30 kg. Sometimes these balls may weigh as much as 50 kg. As soon as the desired size has been obtained, a cut is made with a sharp knife in the side of the ball opposite the handle. This incision is large enough to allow the disc and handle to be pushed out of the ball. The rubber is then dried for some time in the air, a part of the moisture contained in it being "sweated out" in the process. After this drying, the rubber is ready for shipping.

[313] "Culture et Exploitation du Caoutchouc au Brésil," p. 49, Société Général d'Impression, Paris, 1913.

The coagulation of the latex is apparently brought about by the increase in temperature and the action of the chemical agents present in the smoke. According to R. H. Biffen,[314] acetic acid, creosote, and traces of pyridine derivatives are contained in this smoke. The temperature of the smoke is about 65° C., according to G. S. Whitby.[315]

The systems of classification of the different commercial grades of rubber are dependent upon: (1) the botanical source of the rubber, (2) the degree of care used in its preparation, and (3) the region from which it is obtained.

According to the botanical source the rubbers may be classified as:

(1) **Fine Para,** from *Hevea brasiliensis* and *H. Benthamiana*;

(2) **Weak Fine,** from *H. guyanensis,* or from a mixture of this species with one of the above;

(3) **Weak,** from other species of *Hevea.* This rubber is not important commercially.

According to the care used in preparation the following kinds may be distinguished:

(1) **Hard fine Para.** This grade consists of balls obtained by the smoking method, the greatest care being used in their preparation. These balls exhibit on the outer parts a dark brown coloration, which shades into an amber-yellow on the inside. Upon cutting through the balls it can be readily seen that they are made up of numerous concentric layers.

(2) **Medium Para.** Balls prepared by the smoking method with less care and usually containing pasty or spongy places are included in this class.

(3) **Coarse Para (Sernamby, Scrap, Negro heads).** This grade consists of rubber coagulated on the bark or in the vessels used for receiving and collecting the latex. It is pressed together without smoking and is usually very dirty.

According to the region from which they are obtained, it is customary to divide the rubbers into **Islands soft cure,** obtained near the mouth of the Amazon River, and **Upriver hard cure,** which originates near the head waters of the tributaries of the Amazon. The latter is especially prized and commands the highest price of all the grades of rubber on the market.

Preparation by Coagulation with Acetic Acid

Until quite recently, by far the greatest part of the Hevea plantation rubber was coagulated with acetic acid. In the last few years acetic acid has been replaced more and more by formic acid. Since the process is essentially the same with formic as with acetic acid, and since the investigations thus far described in the literature have had to do principally with coagulation by means of acetic acid, this latter coagulant is discussed first in that which follows.

On the plantations of the Middle East, the first step in the manufacture of rubber from the latex which has been brought to a plantation factory is straining to remove various impurities and lumps of rubber formed by spontaneous coagulation during transport. For this purpose screens of metal gauze, or perforated metal plate with holes of different size, are generally used (Fig. 37). As examples may be mentioned screens containing 25, 100 and 150 holes per square centimeter. Devices which greatly hinder plugging of the screens and make exchange of screens easy have recently been recommended.[316]

[314] *Ann. Botany,* **12,** 165 (1898).
[315] *Kolloid-Z.,* **12,** 148 (1913).
[316] *Arch. Rubbercultuur,* **10,** 229 (1926); **11,** 107 (1927).

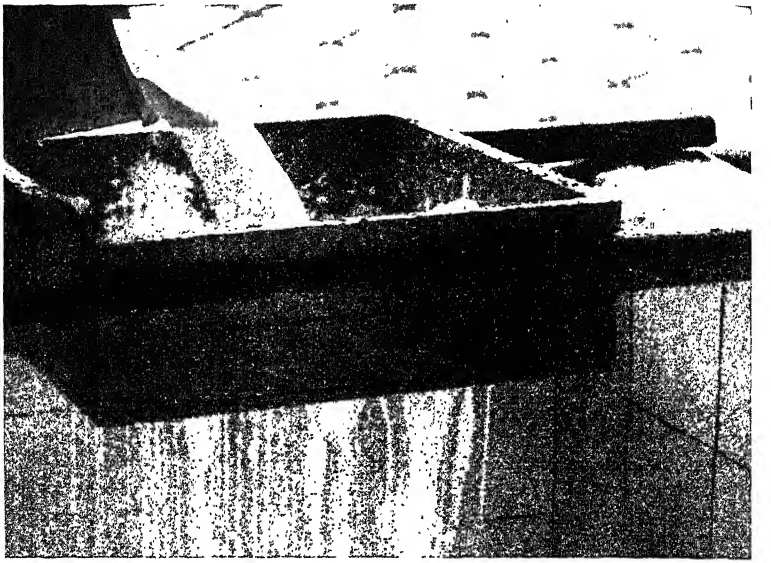


Figure 37—Straining the latex into the coagulating tank.
(From the motion picture film of E. Hauser.)

The filtered latex is then united with other portions of similarly treated latex in a collecting tank or mixing trough. In Java this tank is frequently lined with acid-resisting tile or porcelain-glass. In this container the latex is thoroughly mixed in order to compensate for the probable lack of uniformity in the concentration and composition of portions obtained from different trees. The latex is then diluted with water to the definite concentration desired. For this dilution, and also for the subsequent washing, the purest water available is used. Water which contains slime is to be avoided, or at least must be clarified with alum before being used. Water rich in lime is also said to have a deleterious action. A method for removing the lime from such water has been described by J. C. Hartjens.[317]

Bringing the latex to a definite concentration before the addition of the coagulating material is recommended. The reasons for this step are that the quantity of acetic acid required is dependent on the rubber content, and the properties of the coagulated material and of the vulcanized product prepared from it can vary considerably if the same quantity of acid is not allowed to act upon a latex of the same rubber content. In order to maintain a constant rubber content, the concentration of the thoroughly mixed latex must be determined daily, since this concentration, even in the case of latex from the same planting, can vary greatly with the weather, the age of the trees being tapped, and the frequency of tapping. The methods used for this purpose have already been described on page 60.

The smaller the rubber content of the latex, and the smaller the quantity of acetic acid used, the slower in general is the rate of coagulation. If the decomposition phenomena leading to spontaneous coagulation are avoided, the addition of an insufficient quantity of acid will generally not form a coher-

[317] *Arch. Rubbercultuur*, 4, 397 (1920).

ent coagulum, and the serum will remain clouded by rubber particles or aggregates of particles. The richer the latex is in rubber and the greater the amount of acetic acid added, the greater will be the solidity of the coagulum. On the other hand, the quantity of acid required for coagulation (when calculated on the basis of the amount of rubber produced) seems to be, for all practical purposes, the same for diluted and undiluted latex.

Concentrated latex is coagulated so quickly by the addition of acid in large quantities (if the latex is stirred steadily during the process) that clump formation and non-uniform coagulation can readily take place. Moreover, the difficulty with which air bubbles escape from the coagulum constitutes another disadvantage when concentrated latex is used for the manufacture of sheets. When the coagulation is too slow, or there is too much delay in the manufacture of the rubber, decomposition phenomena capable of altering the properties of the resulting rubber can take place (as is also true in the case of spontaneous coagulation). Therefore, in order to obtain a product of the greatest possible uniformity, it is strongly recommended that on every plantation the same concentration of latex and the same time of coagulation be maintained. The larger plantations should always employ a definite standard method, as has already been done in many cases.

The concentration to be used must be so chosen that the coagulum will receive, in the time available for further working, the most suitable consistency for the purpose in view. In other words, the concentration of latex employed should vary with the product which is to be prepared from the latex. Among these products, only sheets and crepe have a significant role at present. In small factories the preparation of sheets is usually favored, because the machinery required is less expensive. Moreover, the quantity of rubber obtained is about 1 per cent greater than in the case of the manufacture of crepe. Transportation of sheets is cheaper, furthermore, since a case holding 100 kg. of smoked sheets is capable of inclosing only 75 kg. of crepe rubber. In the large establishments the conversion to crepe is more in favor, owing to the simpler and more rapid method of manufacture.

Hevea rubber, obtained by the use of acetic acid, also comes on the market in various other forms to a greater or less extent. The various methods used are described later.

Before going into this matter, however, some information relative to the packing and transportation of the completed rubber will be presented. The packing of the good grades of thoroughly washed plantation rubber is a matter of importance. The room used for the examination and packing of the rubber must be sufficiently well lighted so that exact work is possible, although no direct sunlight should be allowed to fall on the rubber itself. In the packing room, care should be taken to keep out damp air while providing good ventilation. The greatest degree of cleanliness must also be maintained, so that no dust or other impurities can find their way into the rubber.

The boxes used for the packing of rubber were formerly constructed largely of native or imported wood. The wood of the *Abies firma* (the Japanese name is "Momi"), imported from Japan, was especially desired. Before filling with rubber, these cases are well dried in the sun. T. E. H. O'Brien [318] recommends that they be treated on the inside with a 0.5 per cent solution of paranitrophenol before being used.

[318] *Rubber Res. Scheme Bull.*, **42**, 24 (1926).

More recently, veneer chests have come into general favor. The walls of these chests consist of layers of veneer wood glued together, the grain of the outer layers running at right angles to that of the middle layer. By this means a relatively great firmness is obtained with a comparatively small thickness. At present all of the materials necessary for the construction of veneer chests are furnished by the different firms in standard dimensions. Such being the case, the same amount of rubber can be put in every container. The outside dimensions of the chests are usually 19 x 19 x 24 inches, so that 7 chests occupy approximately one cubic meter. The rubber is frequently pressed into these cases by means of presses especially built for the purpose. Too great a pressure is to be avoided, since cracking of the cases and sticking together of the rubber can easily result. In order to utilize the space completely, the crepe and sheet rubber may be previously cut to dimensions corresponding to those of the chests. It is recommended that the chests be filled with 70 kg. of thin crepe, 75 kg. of thick crepe, 100 kg. of smoked sheets, or 65 kg. of the lower grades of rubber.

Before the cases arrive at their final destination, some of them are often damaged more or less during the loading and unloading.[319] In the case of first class rubber which is not to be subsequently washed in the factories, the presence of splinters is especially undesirable. In order to avoid splinters, it is recommended that the sheets or crepe be surrounded by a layer of the same kind of rubber. By this means the material on the inside of the chests is somewhat protected from penetration by splinters of wood. On the other hand, wrapping the rubber in oiled paper and the like is not at all to be recommended, since such materials easily stick to the rubber and can be removed from it only with great difficulty.

In order to hinder the dried rubber from again taking up moisture from the air, it should be packed as soon as possible, and the cases should be closed at once. These latter are then to be carefully marked. Besides the name of the plantation, the kind of rubber, and the net weight of the rubber contained therein, it is desirable that the following warning be added: "Stow away from boilers and the sun."

According to A. van Rossem, packing in mats, which has not been approved for first latex sheets on account of their greater stickiness, is not so objectionable for first latex crepe. Packing in jute bags, which have been powdered on the inside with talcum and starch, is more to be recommended, however. An added advantage of these bags is that they may be sold after use.

Sheet Rubber.* If sheets are to be prepared, the coagulum is generally allowed to form in rectangular "cakes." While undergoing washing, these "cakes" are pressed out without being torn by passing through rapidly rotating, even-speed washing mills. (Fig. 38.) In the case of sheets, a special endeavor is made to have them always of the same thickness, so that uniform drying will result. If the sheets are too thick, the drying is unduly prolonged. On the other hand, sheets which are too thin may be pulled out of shape or even torn apart by their own weight. A regular size of sheet is necessary for satisfactory packing. For the coagulation in the case of the

[319] See van Rossem, A., "Die amerikanische Gummiindustrie und ihre wissenschaftliche Arbeit," (German by M. Pick), Berlin, **1928.**

* Translator's Note. A very excellent discussion of the manufacture of sheet rubber, with particular reference to the economies which have been necessitated by the recent very low price of rubber, is that of R. O. Bishop, "Plantation Sheet Rubber Manufacture," Rubber Research Institute of Malaya, 1932. —V. N. M.

Figure 38.—Milling the coagulum in the preparation of sheets. (From the motion picture film of E. Hauser.)

preparation of sheets, use is made of shallow rectangular vessels of uniform size. Each one of these holds the definite amount of latex which is required for the production of a single sheet. Vessels made of aluminum seem to have been most generally approved. In more recent times, containers of greater size are often used. These are divided by means of regularly arranged partitions into uniform divisions, each one of which yields one sheet.

The sheets are ordinarily smoked during drying (smoked sheets) in order to give them a uniform color and to hinder the formation of molds and bacteria as much as possible.

In the method for the preparation of uniform sheets especially recommended by O. de Vries,[320] the first step is to bring the thoroughly mixed latex to a rubber content of 15 per cent by the addition of water.[321] The purest possible water is used for the dilution as well as for the subsequent washing. For the coagulation, sufficient acetic acid (in the form of a solution having a concentration of about 1 per cent) is added so that each liter of diluted latex receives 0.8 to 1.2 cc. of pure acid. The same amount of latex is always introduced into each coagulating pan. After a few hours, the coagulum has attained a consistency such that it can be handled in the washing mill. The sheets are always put through smooth rolls the same number of times (about 3 or 4), with the rolls at fixed distances. (Fig. 38.) They are then allowed to pass once through a mill with grooved rolls. The ribbed surfaces thus obtained give the sheets an advantage over smooth ones in that the increase in surface makes faster drying possible and the tendency to stick

[320] de Vries, O., "Estate Rubber," p. 326.

[321] A dilution to 20 per cent is more common at present. To each liter of 20 per cent latex is added 1.25 to 1.75 grams of pure acetic acid.

together after drying is less. The distance between the rolls is so regulated that the sheets, after drying, possess a thickness of 3 to 4 mm., measured between the ribs.

According to G. A. Sackett,† who recently returned to America after 3 years in the Middle East, one of the recent developments in plantation practice involves use of sheeting machines in series. Since the machines are synchronized so as to operate continuously on the same coagulum and a certain amount of hand labor is eliminated by having them in series, this arrangement has led to an increase in the capacity of the machines and to a decrease in the cost of making the sheets.

After rolling out, the sheets are allowed to lie overnight in running water,* if such is available, or at least in water which is frequently changed. During this process they must not be packed too closely together. It is essential that the water should have free access to every sheet. By means of this immersion in water, the serum constituents squeezed out of the rubber during contraction are removed. If not removed, these constituents tend to remain on a sheet after drying and give to it a greasy surface. Not only the serum constituents on the surface, but also those in the rubber near the surface, are washed out to some extent in this process. To accomplish the same results, dipping of the sheets in water at 80° to 100° C. has also been suggested. The quality of the rubber is lowered by this latter method, according to O. de Vries.[322]

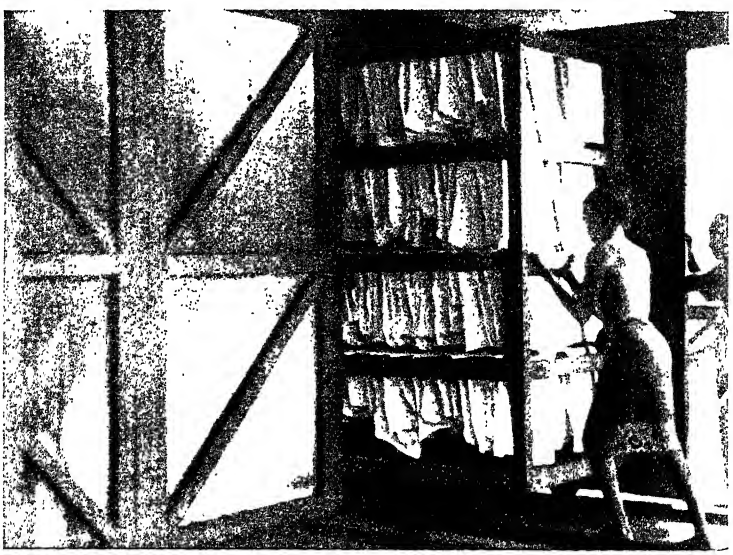


Figure 39—Bringing the sheets into the smoke-house.
(From the motion picture film of E. Hauser.)

On the following morning, the sheets are removed from the water and hung up to drain for from one to three hours, after which they are taken to the smoke house for drying and smoking (*see* Fig. 39). During the first few days in the smoke house, good ventilation should be provided, and the tem-

† Private communication to the translator.

[322] de Vries, O., "Estate Rubber," p. 305.

* Translator's Note. On many modern estates less time is allowed. — V. N. M.

perature should not be too low. The quickest possible drying is necessary, since otherwise the high water content (generally 20 to 30 per cent) will allow chemical changes to take place. The temperature of the smoke house must always be carefully controlled, the optimum temperature being 40° to 50° C. If the temperature rises above 60° C., the sheets frequently become so soft that their own weight causes them to become elongated. The properties of the rubber do not seem to be appreciably changed by exposure to such a temperature, however. For the production of the smoke, use is made of fresh wood, cocoanut shells, etc.

Before transportation the sheets may be brought by trimming to an exactly uniform weight.

In supplementing the previous instructions, it may be mentioned that the use of an anti-coagulant will hinder the spontaneous coagulation of an appreciable part of the latex, which coagulation tends to take place when the weather is hot. In the case of the preparation of sheets, soda is the usual anti-coagulant. For each liter of latex, 5 to 10 cc. of a soda solution (10 grams of anhydrous or 27 grams of hydrated sodium carbonate per 100 cc. of water) are used.

The addition of a bleaching agent, such as sodium bisulfite, is not advisable, since the time of drying is thereby considerably prolonged.

As previously mentioned, the immersion of the sheets in water removes part of the serum constituents. The resulting decrease in the weight of the dried sheets is said by de Vries [323] to be from 1/2 to 3 per cent. The rate of vulcanization of the rubber is simultaneously decreased. If the preservation under water is prolonged, however, an acceleration of vulcanization can again take place. The products of maturation, which are removed only slightly by the water, are the agents which bring about this increase in rate of vulcanization.

The following requirements for a smoke house have been put forward by J. C. Hartjens and E. Goebel:[324] (1) it must stand on dry, well-drained land, be thoroughly ventilated, and be protected against the danger of fire as effectively as possible; (2) the use of smoke-producing materials must be as small as possible; (3) the production of smoke should be so controlled that the smoke will be well distributed. These authors also describe the construction of a satisfactory house.*

As has been shown by A. J. Ultee,[325] an increase in weight of 0.5 to 0.75 per cent occurs during smoking, the increase resulting primarily from the absorption of acetone-soluble compounds. Further drying of the sheets in smoke-free air is not desirable, since such a process would remove a large part of the disinfectant constituents absorbed from the smoke. It is best to pack the sheets on the day they come out of the smoke house.

When sheets have mold on their surfaces, the recommended treatment, according to F. C. van Heurn,[326] is to wipe them off with a damp cloth and then bathe them for a short time in a solution containing 1 volume of formalin in 15 volumes of water. The use of a solution of calcium permanganate for this purpose is reported by P. Arens [327] to yield unsatisfactory results.

[323] *Arch. Rubbercultuur*, **3**, 339 (1919).

[324] *Arch. Rubbercultuur*, **4**, 140 (1920); also see T. E. H. O'Brien, *Rubber Res. Scheme Bull.*, **42** and **44** (1926).

[325] *Meded. Besoekisch Proefsta. Rubberserie*, **No. 31** (1923).

* Translator's Note. For a more recent discussion of the construction of smoke houses, the reader is referred to R. O. Bishop, "Plantation Sheet Rubber Manufacture," p. 44, 60, 61, Rubber Research Institute of Malaya, **1932**.

[326] *Arch. Rubbercultuur*, **5**, 74 (1921).

[327] *Agr. Bull. Federated Malay States*, **5**, 1 (1917).

Crepe Rubber. For the preparation of crepe rubber, the mills used have rolls of uneven speed and are provided with means for continuously washing the rubber. In these mills the coagula are completely torn to pieces, then rolled out into thin sheets for thorough washing, and finally reunited into thick crepes by the milling together of several layers. Crepe rubber also differs from sheets in not having such smooth surfaces and in not usually being smoked.

Since the form and size of the coagula in crepe manufacture are not important, the coagulation is usually carried out in large tanks or other vessels (Fig. 40). A standard dilution of the latex to a rubber content of 15 per cent is recommended. Latex containing 20 or 25 per cent rubber or even undiluted latex can be used, provided the latex from the particular source under consideration does not exhibit very much fluctuation in rubber content.

By regulating the concentration of the latex, the quantity of acetic acid added, and the time before milling, it is possible to bring the coagulum to the consistency most favorable for working. When the mill available is one which can exert no great pressure, a softer coagulum will be necessary than when a stronger mill is used.

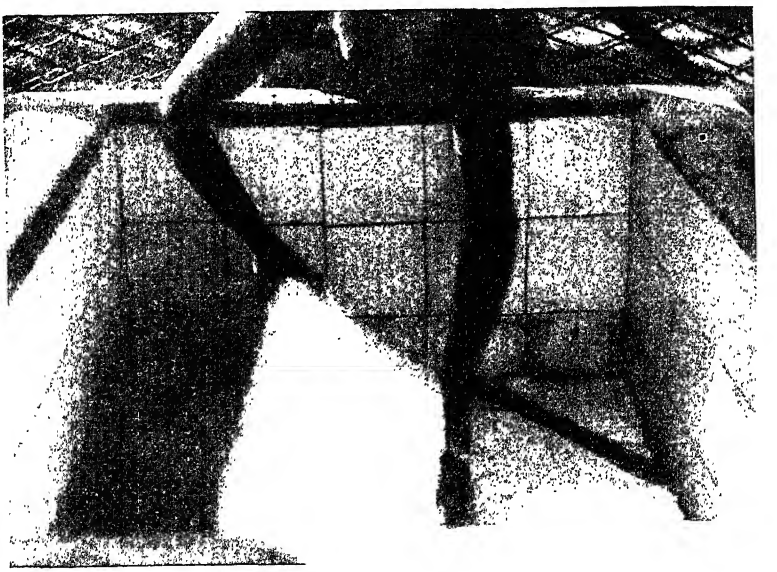


Figure 40—Removing the coagulum from the coagulating tank.
(From the motion picture film of E. Hauser.)

According to the standard method recommended by O. de Vries,[328] the latex is first thoroughly mixed and then diluted to a rubber content of 15 per cent. Sufficient sodium bisulfite is added to bring the concentration of this salt to 1/2 to 1 gram per liter of diluted latex. The sodium bisulfite prevents the later darkening of the rubber and also exerts a disinfectant influence. Although the time of drying is increased by this treatment, it is not a matter of consequence, as crepe rubber is naturally rapidly drying.

[328] de Vries, O., "Estate Rubber," p. 283.

For the coagulation a 5 per cent solution of acetic acid is added to the diluted latex (final concentration of undiluted acetic acid—0.6 to 1.0 cc. per liter of latex). In order to distribute the coagulating agent uniformly through the latex, thorough stirring during and immediately after mixing is recommended. By following these directions there is obtained a coagulum which is ready for further working, either on the same day or early the next morning. It is recommended in this connection that approximately the same time should always be allowed, although latex treated with sodium bisulfite does not yield rubber easily injured by variation in the time elapsed before the coagulum is worked.

As previously mentioned, the further processing of the coagulum is carried out on a mill having rolls which rotate at uneven speed. The coagulum is torn into pieces under a spray of water, which prevents the development of too much heat. De Vries [329] states that heating to 50° C. is not deleterious to the rubber. The various parts of the coagulum are rolled out into thin pieces of crepe. These are subsequently milled together more or less into a heavier crepe, which should have, after drying, a thickness of about 1 to 2 mm. (*see* Figs. 41 and 42). The extent of the working of the rubber between the washing rolls appears to have little effect on its quality.

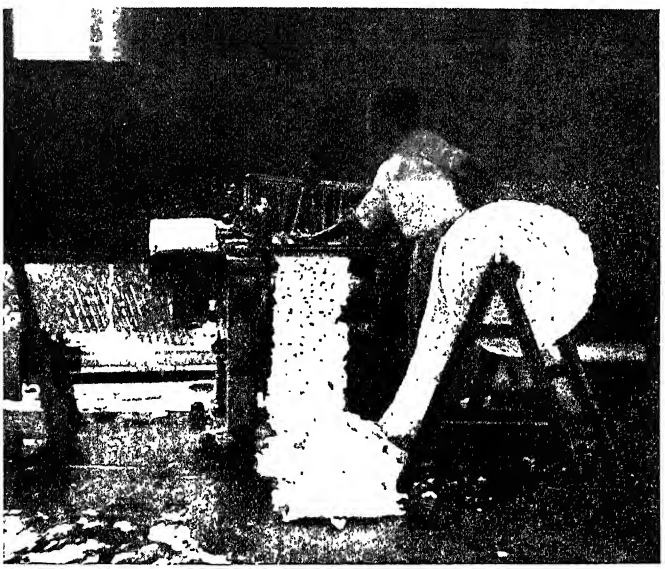


Figure 41—Milling and washing the coagulum in the case of the production of crepe rubber.
(From the motion picture film of E. Hauser.)

It is not necessary to soak crepe in water after milling, since it is washed so much more thoroughly than sheets during the milling process.

Since crepe rubber, when delivered from the mills, contains relatively little water (generally 10 to 20 per cent) and is, as a consequence of its porous structure, faster drying than sheets, decomposition reactions during drying are not much to be feared. Crepe rubber can therefore be dried at room

[329] de Vries, O., "Estate Rubber," p. 271.

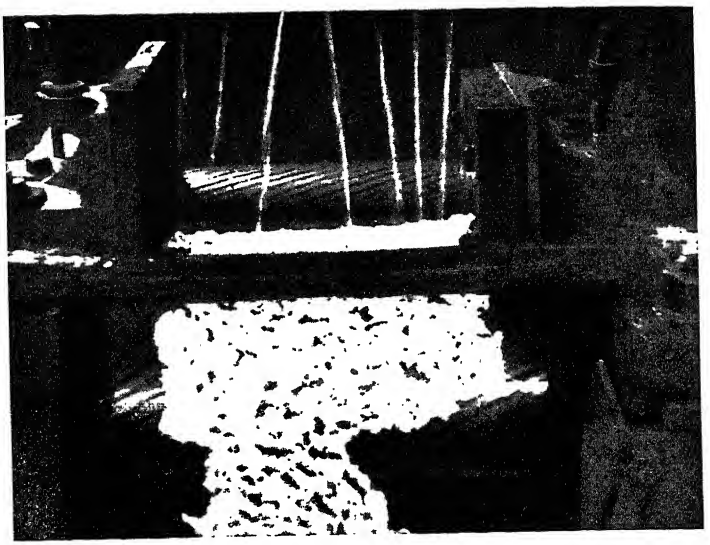


Figure 42 (Above)—Milling and washing the coagulum in the preparation of crepe rubber.
(From the motion picture film of E. Hauser.)

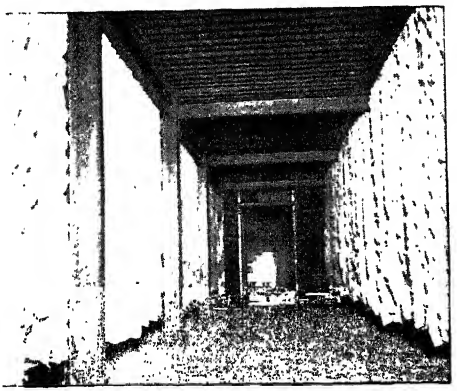


Figure 43 (Left)—Drying room for crepe rubber.
(Courtesy of E. Hauser.)

temperature in well ventilated rooms from which sunlight is excluded. (*See* Fig. 43.) Warm air at a temperature of about 50° C. is, however, often introduced into the drying house to accelerate the drying of the rubber and to prevent bacterial infection and the formation of molds. Vacuum chambers are also used for drying, although this method seems to have been largely abandoned since the advent of the sodium bisulfite treatment.

When, in the manufacture of crepe, it is desired to carry out the coagulation every second day rather than every day, it is necessary, according to O. de Vries and N. Beumée-Nieuwland,[330] to add 0.07 per cent of ammonia to the latex in order to prevent premature coagulation. The extra costs arising from this ammonia and from the additional acid required for coagulation may be greater than the savings in factory operation which are made possible by the delay.

[330] *Arch. Rubbercultuur*, **11**, 317 (1927).

Biscuits. In earlier days, before the use of machinery had become general, a considerable part of the plantation rubber was prepared by coagulating the latex in circular pans and freeing the resulting flat coagula from serum as completely as possible by pressing them on level tables with wooden rollers, bottles, etc. "Biscuits" is the commercial name for the round cakes of rubber thus obtained. At present they are only prepared by the natives, and on plantations so small that the establishment of a large factory would not pay.

Blanket Crepe and Sole Crepe Rubber. In order to save space during transportation, thin layers of crepe are sometimes pressed together, after drying, into "slabs" having a thickness of 4 to 5 mm. This pressing together is preferably carried out under a stream of water in order to prevent the rubber from becoming too hot. The thin layers of crepe dried under vacuum are usually also milled together to some extent.

The unvulcanized crepe used for shoe soles is prepared from thin crepe in a similar manner.[331] The preparation of sole-crepe, which originated in Ceylon during the war, has become a matter of greater importance in recent years. The usual standard dimensions of sole-crepe are 13x16 inches. The thickness may be 1/8, 3/16, 1/4 inch or greater. A uniform, clear, light color is one of the primary requisites of a good sole-crepe.

Block Rubber. Block rubber is usually prepared by pressing together, while still warm, crepe rubber which has been dried under a vacuum. Special block presses, producing blocks with a thickness of about 5 cm., are used. These blocks are convenient for transportation, but possess the disadvantages of having to be cut up again before use, and of being difficult to examine for impurities, especially when they have large dimensions.

At the present time, rubber which retains moisture tenaciously is often worked up into blocks. When the water content of these is large, there may occur decomposition reactions, which tend to result in a more rapid rate of vulcanization. The addition of creosote, etc., is recommended for the purpose of preventing putrefaction. Whether this type of rubber possesses advantages over sheets and crepe for certain uses does not seem to have been established with certainty.

Slab Rubber. At times, rubber is brought into the market in the form of cakes 1 to 2 cm. thick (slab rubber). This rubber is obtained by allowing the coagulum to pass once or twice through a mill with rolls of even speed, which are set rather far apart. Only a small proportion of the serum is expelled by this process. After surface drying, 10 to 12 per cent of water remains in the slabs. The ensuing maturation process (*see* p. 102) leads to the formation of natural accelerators. According to W. Spoon,[332] longer preservation of the slabs in the tropics permits of considerable decomposition, with eventual tackiness developing on the surfaces, while the inner portions remain practically unchanged in properties. The disadvantages of slab rubber are that considerable power is required to sheet it out, and the sheets so produced are slow in drying. This type of rubber appears on the market but rarely.

The By-Products and Their Handling. Although most of the latex is handled according to the methods described above, some of it is unavoidably coagulated at the tree or during transportation from the tree to the factory. Varying somewhat with the method of handling, the coagula are more or

[331] *India Rubber World*, **69**, 791 (1924). [332] *Arch. Rubbercultuur*, **11**, 73 (1927).

less contaminated with foreign matter and lacking in uniformity. A usable rubber can nevertheless be prepared from most of these by-products. They may be divided into the classes described in the following paragraphs.

"Scrap" is the designation of that kind of rubber which is formed by the drying out of the latex on the bark at the tapping cut. It can be collected either on the day it is formed (in which case a further flow of latex is often excited) or preferably on the following morning, immediately before a new cut is made. This kind of rubber is variable in color and quality.

The latex which drops from the tree or is spilled from the cups on the ground yields the so-called "earth" rubber which, even after washing, is mixed with sand. Since this rubber is not collected every day it is ordinarily lacking in uniformity and is of small value.

The rubber which can be recovered from the strip of bark removed in tapping is known as "bark" rubber. It is obtained not only from the inner part of the strip of bark, but also, to a considerable extent, from the residue of rubber remaining on the bark after removal of the "scrap" rubber. On many plantations, the strips of bark must be delivered by every tapper, a check on the accuracy with which he has followed directions being thus possible. The bark is usually finely ground in a macerating machine under a considerable stream of water. The bark particles are floated away and the rubber is pressed together by this process. The rubber thus obtained is generally mixed with pieces of bark, and is of smaller value than "scrap" rubber.

"Lump" is the term applied to coagulated rubber removed from the latex by the strainer. It consists chiefly of rubber formed by evaporation and by spontaneous coagulation and is usually contaminated with pieces of bark, leaves, insects, etc. Its color varies from yellow to dark brown.

Rubber obtained from the scum which collects on the surface of the coagulation tank is designated as "scum" rubber. This scum must be removed, particularly in the case of the preparation of sheets, since no bubbles of air should be introduced into these sheets. A rubber having good properties is obtained by treating the removed scum with acetic acid. This rubber usually has a dark and irregular color, however. Less satisfactory properties are exhibited by the rubber obtained from the scum which forms immediately after the addition of acetic acid to the latex. This scum generally contains flocculated rubber to some extent.

When the collecting vessels are not washed out in the factory, a layer of rubber, known as "cup film," is usually formed by evaporation. Such rubber exhibits properties similar to those of "scrap" rubber.

Upon cleaning the vessels used for collecting and handling the latex there is obtained a contaminated, diluted latex, which can be coagulated with acetic acid. The quality of the rubber (designated as "washings") thus obtained is generally far from uniform. If it has not been too greatly contaminated by earth, muddy water, etc., this rubber may possess fairly good properties.

The by-product rubbers mentioned above are ordinarily worked into crepe, a specially constructed scrap-washer now being used for the purpose. Products of similar quality may be segregated before handling, or all types may be mixed together on this washer. "Earth" rubber, which often tends to become soft and gelatinous, is kept separate from the others. The rubber obtained by the combination of mixed by-products is called "compound" rubber or "compo."

Use of Other Coagulating Agents

Numerous investigators have interested themselves in the possibility of replacing acetic acid by some other coagulating agent. Since the action of acetic acid has been studied in such detail, and since this acid, when properly used, yields a first-class product, other coagulants are able to come into use only when they can either produce a more suitable rubber for the industry, or for some particular use at least, or when they can yield a rubber just as good at a lower price. A further requirement of a satisfactory coagulant is that slight variations in the quantities used (a circumstance difficult to avoid in practice) should not result in a lack of uniformity in the product.

In considering the coagulating agents which have been recommended for use in place of acetic acid, first mention should be given to formic acid, which is now used more extensively than acetic acid in the Netherlands East Indies. The salts of fluosilicic acid have also been used to some extent.

Since it is felt that a review of experiments with other coagulants should be of some practical interest, a survey of all such agents is presented below. Before discussing them individually, it should be mentioned that the strong acids coagulate latex completely, whereas most alkalies (ammonia, for example) protect against coagulation, and salts coagulate only at high concentrations. Table 5, which was compiled by P. Schidrowitz,[333] summarizes the values reported by different authors for the quantities of various coagulants required to produce complete coagulation of one liter of latex containing 30 per cent of rubber.

TABLE 5.—*Coagulating Effect of Various Substances.*
(No. grams of coagulant per liter of 30 per cent latex.)

	Eaton	Morgan	Parkin	Beadle & Stevens
Acetic Acid	1.0	1.0	9.5	1.5 - 6.0
Formic Acid	0.6	0.8	4.5	
Hydrochloric Acid	0.7	0.7	1.0	0.4 - 0.5
Hydrofluoric Acid	0.5	0.5		
Nitric Acid	1.0	1.0	3.0	
Sulfuric Acid	0.9	1.0	1.0	0.5 ->10
Calcium Chloride	5.0	5.0		
Ammonium Sulfate	10.0	10.0		
Tannic Acid	1.0	1.0		
Oxalic Acid		2.0		
Tartaric Acid		2.5		
Citric Acid		5.0		

The discussion which follows provides further information regarding the action of the individual reagents.

Formic acid. According to O. de Vries,[334] the quantity of acid required for a similar coagulation is three-fourths as great in the case of formic as compared to acetic acid. Formic acid yields a rubber somewhat lighter in color. Although it has been claimed that formic acid also has an antiseptic action, this claim was not substantiated by B. J. Eaton,[335] who found the quantity of acid remaining in the coagulum to be reduced by washing to such a small trace that it had no influence on molds or bacteria. The physical properties and the resistance to aging of rubber made with formic acid were found by O. de Vries, W. Spoon and R. Riebl [336] to be substantially the

[333] "Rubber Recueil," 370.
[334] de Vries, O., "Estate Rubber," p. 180.
[335] *Dept. Agr. Federated Malay States, Sp. Bull.*, No. 17, 16 (1912).
[336] *Arch. Rubbercultuur*, **9**, 763 (1925); **11**, 354 (1927).

same as those of rubber made with acetic acid. In coagulating with formic acid, O. de Vries [337] observed in some cases a rather irregular behavior, which was perhaps attributable to the content of formaldehyde in the acid.

How extensive the use of formic acid in the Netherlands East Indies has become is demonstrated by the statement of de Jong [338] to the effect that 184 tons of formic acid and only 75 tons of acetic acid were imported for use on the East Coast of Sumatra in 1927. In this same territory, according to D. F. van der Burg,[339] 80 per cent of the plantations were using formic acid in 1927, the reason being that small savings apparently result from the substitution of this agent for acetic acid. This investigator stated that the apparent savings were only an illusion, since his experiments indicated the corrosion of metal parts (such as rolls, coagulating tanks, etc.), with which the formic acid comes in contact, is much greater than is the case with acetic acid. It seems not improbable, therefore, that formic will gradually be replaced once more by acetic acid.

Oxalic, lactic, tartaric and **citric** acids also seem capable of yielding good rubber. As a consequence of their higher prices, they have so far been used very little. Furthermore, the properties of the products obtained have not been investigated thoroughly.

By the use of **tannin** there are precipitated certain serum constituents which remain in solution in the case of coagulation with acetic acid. This method appears so far to have found no place in plantation practice. B. J. Eaton [340] states that its use leads to a pronounced darkening and oxidation of the rubber.

Sulfuric acid appears to offer no particular advantage over formic acid. The quantity of sulfuric acid required to coagulate one liter of latex (rubber content of 15 per cent) amounts to 0.45 to 0.6 gram, according to O. de Vries.[341]

The recent low price of rubber and the consequent necessity for economy have prompted J. L. Wiltshire [341a] to reopen the question of using sulfuric acid as a coagulant for latex.* His experiments indicate that the cost of coagulation by means of this acid is but one-half of that with formic acid and only one-third of that when acetic acid is used. For several reasons, a small quantity of acid (about 2.7 grams of pure acid per pound of dry rubber) was found to be most suitable. Although Wiltshire found it possible to produce rubber of good quality with this agent, provided sufficient care was exercised, his realization of the prejudice existing against such a procedure prevented him from making a direct recommendation in favor of sulfuric acid as a coagulant.

Hydrofluoric acid was recommended as a coagulating agent by D. Sandmann,[342] and was put on the market under the name of "Purub." The rubber produced by this agent is said by F. Frank [343] to be characterized by a rapid rate of vulcanization. The high price and strongly corrosive action of "Purub" has militated against its adoption by the industry.

Sulfurous acid, which can be introduced into the latex from a tank or by burning sulfur and passing in the fumes, seems to yield good rubber, according to O. de Vries.[344] The determination of the exact quantity of this material to be used is not an easy matter.

[337] de Vries, O., "Estate Rubber," p. 180.
[338] *India Cultures*, **12**, 1035 (1927).
[339] *India Cultures*, **13**, 161 (1928).
[340] *Dept. Agr. Federated Malay States, Sp. Bull.* **No. 17**, 17 (1912).
[341] de Vries, O., "Estate Rubber," p. 176.
[341a] *J. Research Inst. Malaya*, **4**, 94 (1932).
* Translator's note by V. N. M.
[342] *Tropenpflanzer*, **14**, 189 (1910).
[343] *Gummi-Ztg.*, **22**, 1404 (1908).
[344] de Vries, O., "Estate Rubber," p. 186.

Hydrochloric and **nitric** acids, on the other hand, produce inferior rubbers. **Boric** and **hydrocyanic** acids do not bring about complete coagulation.

Although **carbon dioxide** was recommended as a coagulant by W. Pahl,[345] complete coagulation is not accomplished by this substance.[346]

Of the salts which have been tested, **sodium silicofluoride,** which was recommended several years ago by J. Edwardes,[347] appears thus far to have been the best. It is already used to a considerable extent. A cheaper price than acetic acid and a certain degree of protection against molding and against the formation of air bubbles are the advantages claimed for this substance. According to H. P. Stevens,[348] coagulation with sodium silicofluoride yields a rubber having a greater resistance to aging than rubber made with acetic acid.

N. H. van Harpen [349] recommended a solution of sodium silicofluoride containing a small quantity of formic acid as a coagulant. Less formation of bubbles and of mold is said to take place when this mixture is used in coagulating latex. Furthermore, the subsequent darkening of crepe is less than when formic acid is used. Smoked sheets show a darker color, however, when made with this substance. Coagulation vessels of aluminum cannot be used with sodium silicofluoride. On the other hand, zinc is a satisfactory metal for such vessels, inasmuch as it is attacked no more by this salt than by formic acid.

According to L. R. van Dillon, C. Knaus, G. M. Kraay and R. Riebl,[350] satisfactory coagulation by means of sodium silicofluoride is obtained with diluted latex only. Even with latex containing but 15 per cent of rubber, the coagulation was generally still incomplete upon standing one day. With latices containing 12 per cent or less of rubber the coagulation was complete on the following day, at least, and sometimes even after a few hours' standing. In the case of 12 per cent latex, the requirement of sodium silicofluoride is 7 to 10 grams per kilogram of dried rubber. It is reported by A. W. K. de Jong [351] that latex with a rubber content of 20 per cent can be coagulated with sodium silicofluoride, provided use is made of a heated solution or of one to which formic acid has been added. In this connection, T. E. H. O'Brien [352] recommended that for the preparation of sheets from latex which has been diluted to 1.5 pounds of dry rubber per gallon, 8 parts of sodium silicofluoride and 1 part of formic acid be used for each 1600 parts of latex.

According to A. J. Ultee,[353] **magnesium silicofluoride,** which has a greated solubility than the sodium salt, is also of value.

Zentgraaf [354] and W. Spoon [355] report that **alum** is used for the coagulation of latex by the natives of Sumatra. Latex which has been diluted with an equal volume of water requires 3 to 4 grams of alum per liter for coagulation, whereas that which has been diluted with 9 volumes of water needs but 0.75 to 1 gram for each liter of diluted latex, according to O. de Vries and N. Beumée-Nieuwland.[356] Spoon states that the only disadvantage of rubber prepared with alum is its slow rate of vulcanization. The non-

[345] See "The Rubber Industry" (ed. by J. Torrey and A. S. Manders), p. 234, The International Rubber and Allied Trades Exhibition, Ltd., London, **1911.**
[346] Compare de Vries, O., "Estate Rubber," p. 187.
[347] *Arch. Rubbercultuur,* **7,** 202 (1923).
[348] *Bull. Rubber Growers' Assoc.,* **8,** 345 (1926).
[349] *Arch. Rubbercultuur,* **10,** 602 (1926); **11,** 477 (1927); **12,** 423 (1928).
[350] *Arch. Rubbercultuur,* **12,** 61 (1928).
[351] *Arch. Rubbercultuur,* **12,** 191 (1928).
[352] *Trop. Agr.,* **70,** 235 (1928).
[353] *Mededeel. Besoekisch. Proefsta. Rubberserie,* **No. 1,** 26 (1917).
[354] *Rubber en Thee Tijdschrift,* **9,** 379 (1924).
[355] *Arch. Rubbercultuur,* **9,** 555 (1925).
[356] *Arch. Rubbercultuur,* **11,** 518 (1927).

uniform product was formerly shipped almost exclusively to Singapore, where it was worked by the Chinese into blanket crepe having a thickness of 6 to 9 mm. ("remilled rubber"). Rubber of this kind is graded according to color as light brown, brown, darker brown, and black brown. Factories for the preparation of this native rubber are also in operation in Sumatra. According to W. Spoon,[357] the number of such plants has increased considerably in recent years.

The possible value of certain other salts as coagulating agents has also been investigated. Information regarding the usefulness of **sodium bisulfate, sodium sulfate, sodium chloride, calcium chloride,** and **mercuric chloride** has been compiled by O. de Vries.[358]

Cream of tartar was recommended by T. Petch [359] for the coagulation of latex. Although products made from the rubber thus obtained are said to have good properties, this coagulating agent seems not to have been adopted.

Aluminum lactate, recommended as a coagulant by C. H. Boehringer-Sohn,[360] yields a poorer rubber than does acetic acid, according to W. Spoon.[361]

Hydrogen sulfide is said by G. S. Whitby [362] to be incapable of bringing about coagulation, either when added as a saturated solution or when introduced as a gas until saturation has been reached. In fact, this investigator demonstrated that it is an anti-coagulant, since the latex samples treated with it were not coagulated after standing 118 hours.

Hydrogen peroxide has a retarding effect on coagulation when added in small quantities (1 cc. H_2O_2 of 30 volume per cent for each 200 cc. of 10 per cent latex), according to G. S. Whitby.[362] It favors coagulation at higher concentrations.

Alcohol cannot be used commercially as a coagulant, because too large a quantity is required for complete coagulation. O. de Vries and N. Beumée-Nieuwland [363] state that one-half volume of 96 per cent alcohol will rapidly produce complete coagulation. Although latex diluted with an equal volume of water can be coagulated by an equal volume of alcohol, latex diluted with 2 volumes of water cannot be completely coagulated by 2 volumes of alcohol. When diluted with 9 volumes of water, the latex can no longer be coagulated by alcohol at all. The addition of common salt or alum to latex diluted with 4 volumes of water will allow it to be coagulated by means of one-half volume of alcohol.

In laboratory experiments, alcohol serves as a very satisfactory coagulant, since it accomplishes a rapid and complete coagulation when added in sufficient quantity. It is of interest to mention that the nitrogenous constituents of the serum are precipitated less completely by alcohol than by acetic acid. According to de Vries,[364] heating will precipitate 1/4 per cent of proteins from the serum remaining after coagulation with alcohol, as compared with 1/6 per cent in the case of acetic acid.

The juice of the fruit of the *Carica Papaya* is capable of coagulating either fresh or preserved latex, according to A. J. Ultee.[365]

A 1 per cent solution of this dried juice is twice as effective for coagulation as a 1 per cent solution of acetic acid. This same experimenter states [366] that

[357] *Ind. Merc.*, **51**, 253 (1928).
[358] de Vries, O., "Estate Rubber," p. 188.
[359] [illegible] of
[360] *Kolloid-Z.*, **10**, 40 (1915).
[361] *Arch. Rubbercultuur*, **6**, 144 (1922).
[362] *Kolloid-Z.*, **12**, 147 (1913).
[363] *Arch. Rubbercultuur*, **11**, 518 (1927).
[364] de Vries, O., "Estate Rubber," p. 216
[365] *Teysmannia*, **28**, 179 (1917).
[366] *Arch. Rubbercultuur*, **2**, 343 (1918).

rubber obtained by using papain shows normal physical properties, but a very high viscosity. It dries very slowly.

The serum which may be withdrawn from the coagulum in the case of coagulation with acetic acid still contains considerable acid and may be used as a coagulating agent on the following day. Some pure acetic acid is usually added to the serum in such a case. The quality of the rubber thus obtained does not differ appreciably from that of ordinary rubber. Decomposition of the serum is retarded by the addition of sodium bisulfite. When using serum, it is always difficult to determine just how great the coagulating effect will be. The use of pure acetic acid is therefore to be preferred under normal circumstances.

The natives also use as coagulants fermented cocoanut milk, fermented pineapple juice, and the liquids obtained by the fermentation of juice from red coffee berries, cocoa beans, etc. O. de Vries [367] states that rubber obtained with such agents is satisfactory, although not as uniform as the product resulting from the use of acetic acid.

The last coagulating medium worthy of mention in this discussion is urine, which is said by Zentgraaf [368] to be used by the natives of Sumatra.

Methods of Preparation Involving the Use of No Coagulating Agents

Spontaneous Coagulation. Spontaneous coagulation has been repeatedly recommended as a method of manufacture of crude rubber (*see* p. 103). This method, since it tends towards non-uniformity, does not seem to be suitable for the production of standard grades. The attempt has been made to regulate the process by adding cane sugar (about 1.5 to 3 grams per liter of the undiluted latex) to give a uniform production of acids. The methods which have been tried for the prevention of surface discoloration and mold formation include (1) excluding the air from the coagula, which project from the serum, by immersing them once more, and (2) adding disinfectants such as sodium sulfite, creosote, beta-naphthol, etc. Spontaneous coagulation is greatly accelerated by the addition of small quantities of calcium chloride, according to L. E. Campbell.[369] Barium and magnesium chlorides, on the other hand, have a coagulating effect only at higher concentrations. Spontaneous coagulation is greatly retarded, or even stopped, by calcium oxalate or sodium fluoride in the proper proportions.

At the present time, spontaneous coagulation is only used in certain small factories and by the natives. The coagula are most easily converted into slab rubber (*see* p. 119).

Kerbosch Process. In the process developed by M. Kerbosch, a marked evaporation of the water in the latex is brought about by a current of warm air. According to O. de Vries [370] and E. A. Hauser,[371] the first step in the process is to put the latex into a drum (about 2 m. in diameter and 1.8 m. in length) which can be put in slow rotation around its horizontal axis. Along the axis of the drum is a tube provided with many small openings, through which a strong blast of air is blown. Stirring vanes rotating in the direction opposite to that of the drum serve to distribute the air stream. The drum, while rotating, takes up a thin layer of latex, which dries out almost completely in a half revolution. At the end of a full revolution another layer is taken up on the dry under-layer. In this manner all of the latex is finally dried. The

[367] de Vries, O., "Estate Rubber," p. 197.
[368] *Rubber en Thee Tijdschrift*, **9**, 379 (1924).
[369] Campbell, L. E., "Rubber Research In Ceylon," p. 115, Columbo, **1918.**
[370] de Vries, O., "Estate Rubber," p. 436.
[371] Hauser, E. A., "Latex," p. 100, Th. Steinkopff, Dresden and Leipzig, **1927.**

temperature of the latex should not rise above 40° C., since otherwise flocculation or clotting can easily take place.

Since all of the serum constituents are retained in rubber made by this process, its weight is 10 to 12 per cent greater than that of rubber prepared from the same quantity of latex by the acetic acid method. The water content of Kerbosch rubber is relatively great (varying from 3 to 9 per cent), as a consequence of the hygroscopicity of the serum constituents present.

On account of its small serviceability and the difficulty of controlling it in practice, the Kerbosch apparatus has not been adopted to any extent. The fact that the opinions expressed regarding the properties of the rubber obtained have not always been favorable has also militated against the use of the Kerbosch process.

Dilution and Centrifuging. As shown by J. Parkin [372] years ago, Hevea latex cannot be coagulated merely by dilution. Furthermore, only creaming takes place upon the dilution of latex which is already in a flocculated condition (as a consequence of spontaneous coagulation, for instance).

H. A. Wickham,[373] J. Parkin,[374] M. K. Bamber,[375] and C. Beadle and H. P. Stevens [376] state that the rubber cannot be completely removed from latex by centrifuging. On the other hand, the rubber in latex which is preserved with formaldehyde, or to which a small amount of acetic acid has been added, can be brought into an agglomerated state by centrifuging.

Smoking Process. Although the Brazilian smoking method (*see* p. 108) has been used experimentally on various plantations in Netherlands East Indies, and has been recommended to the natives, it has not been adopted. Several years ago, D. MacGillavry had a whole year's output from two plantations (about 100 tons) prepared in this manner. The smoking took place in large sheds, in each of which 40 iron smoking ovens were set up. The cost of preparation of this rubber was about the same as that for sheets and less than that for crepe. According to the investigations of O. de Vries and W. Spoon,[377] and the expert opinions of several manufacturers, the properties of rubber of this type are quite satisfactory, being intermediate between those of normal sheets or crepe and those of hard fine Para. Nevertheless, this rubber, known as "Java-Para," has not come into favor. Even MacGillavry has abandoned the use of the smoking method. Dominikus [378] has described and illustrated several pieces of apparatus, which were constructed according to the suggestions of Coutinho, van der Kerkhove, Wickham, Brown and Davidson, Macadam and da Costa, and in which the latex is coagulated by introducing smoke. None of these seem to have been used very much commercially. The Ripeau [379] process also has not come into favor.

Sprayed Rubber. Although G. Krause [380] was the first to dry latex successfully by a spraying process on an experimental scale, it was through the efforts of E. Hopkinson [381] that spray drying was developed to the point where it could find extensive use on the plantations of the Middle East. In this process, the latex falls on a rapidly rotating disc in the upper part of an inclosed drying chamber. The latex is thrown out in the form of a fine mist by centrifugal force. A strong current of hot air entering at the top of the

[372] *Roy. Botan. Gard. Ceylon, Circ.*, **1**, 144 (1899).
[373] Wickham, H. A., "On the Plantation, Cultivation and Curing of Para Indian Rubber," p. 63, London, 1908.
[374] *Roy. Botan. Gard. Ceylon, Circ.*, **1**, 144 (1899).
[375] *Ibid.*, **3**, 297 (1906).
[376] *Kolloid-Z.*, **13**, 210 (1913).
[377] *Mededeel. Proefsta. Rubber*, **No. 8** (1927).
[378] *Gummi-Ztg.*, **22**, 926 (1908).
[379] See Hauser, E. A., *ibid.*, **41**, 1163 (1927).
[380] See Hauser, E. A., "Latex" p. 103, Th. Steinkopff, Dresden and Leipzig, **1927**.
[381] *Gummi-Ztg.*, **41**, 1223 (1927).

chamber rapidly vaporizes the water in the latex mist, so that dry rubber settles to the bottom in the form of a fine "snow." The spongy mass of "snow" is pressed together for transport.

In contrast to the sheet and crepe rubber obtained by coagulation, sprayed rubber possesses the advantage of a 6 to 6.5 per cent greater yield, as a consequence of the retention of all the serum constituents. It also vulcanizes much faster. The vulcanizates prepared from it have good mechanical properties and withstand aging satisfactorily. The power requirement for its mastication is high, since this rubber has great "nerve" and toughness. By the addition of protective colloids such as glue, a sprayed product, which is pulverulent and which can easily be molded, is obtainable.[382]

Electrophoretic Process. The electrophoretic (electrodeposition) process[383] depends on the fact that, upon passage of an electric current, the rubber particles in latex migrate towards the anode and are deposited thereupon in the form of a homogeneous film. In order to prevent the formation of oxygen bubbles in the rubber deposit, the anode may be surrounded by a porous diaphragm, on the outside of which the rubber collects, while the bubbles form only on the inside. Use can also be made of metal anodes, if the formation of bubbles of oxygen is avoided by some method. H. Baclesse[384] has described various arrangements suitable for carrying out this process on a practical scale. According to Baclesse, colloidal sulfur, accelerators and dyestuffs can be mixed with the latex. A current density of 0.08 amp./ sq. cm. has been specified as a suitable one. The rubber deposit can be built up to the extent desired, a thickness of 1 mm. being obtainable in a few minutes.

The process is capable of broad application, and, since the resulting rubber is subjected to but very little mechanical treatment, the products obtained naturally possess very good physical properties.

Emka Process. According to E. Hauser,[385] the Emka process, so named from the initials of the discoverers, van der Marck and Kremer, is carried out as described in the next paragraph.

The previously strained latex, to which sodium bisulfite has been added, is coagulated in flat pans, as in the preparation of sheets, the coagulant being acetic or formic acid. The flat cake obtained by rolling out the coagulum with a hand roller is then folded over transversely. The edges are pressed together by means of the fingers or a small hand roller. Only at one place along the edges is an opening left, the purpose of this opening being to allow the introduction of a rubber tube, which is in turn attached to a bicycle pump. By this means, it is possible to inflate the sack formed from the rubber cake to such an extent that it gradually takes on the form and appearance of an oblong rubber balloon. At this point, the opening used for the introduction of air is also closed, and the balloon is hung up to dry. After the drying, which is said to be complete in a few hours, the balloon is cut open, and the surfaces are covered with talcum. The thickness of the membrane may be varied more or less by controlling the volume of air introduced. An exact determination of the extent to which this process can be advantageously used has not yet been made.

[382] See Davey, W. C., *India Rubber J.*, **70**, 985 (1924).
[383] See *India Rubber World*, **75**, 127 (1926) and *Trans. Inst. Rubber Ind.*, **4**, 343 (1928).
[384] *Kautschuk*, **2**, 68 (1926).
[385] *Gummi-Ztg.*, **41**, 1162 (1927).

MANIHOT

In the case of *Manihot Glaziovii,* the latex is either coagulated immediately on the tree (Lewa method, *see* p. 71) or collected in liquid form.

Lewa Method

In the Lewa Method the coagulating agent, which is applied to the bark, must have such a rapid coagulating action that the latex flowing out of the wound on the tree cannot spread out laterally. (Fig. 44.) A further requirement is that the latex should have, before drying, such a consistency that the resulting rubber can be easily collected in the form of strips.

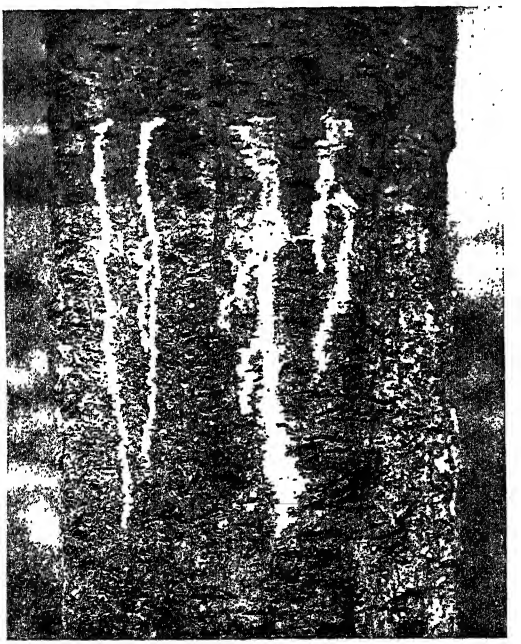


Figure 44—Portion of the trunk of a *Manihot Glaziovii* tree tapped according to the Lewa method; with required quantity of coagulant on the left; with insufficient coagulant on the right.

Attention is also called to the fact that, in the case of the Lewa method, the most desirable concentration of the coagulating agent can vary somewhat with the age of the tree, the climatic conditions, and the frequency of tapping. In every case, it is easily possible to determine the best concentration by means of preliminary experiments. Whenever the concentration of coagulant is insufficient, the collection of the rubber is considerably more difficult.

In German East Africa, the coagulating agents used in the early days consisted exclusively of the juices of certain citrous fruits. In fact, the trunk of the tree usually was merely rubbed with the partly peeled fruit. As was demonstrated by C. Kinzelbach and A. Zimmermann,[386] the juice of the wild orange gives a good coagulation even after dilution with three volumes of water. A solution prepared from the dried fruit pulp of the *Adansonia digitata* was later used considerably as a coagulant. The concentration of this agent to be used was determined by C. Kinzelbach.[387]

nzer, **5,** 25 (1909).

[387] *Pflanzer,* **5,** 169 (1909).

According to the investigations of C. Kinzelbach and A. Zimmermann,[388] juice pressed out of the leaves of the Sisalagave can serve as a coagulant after the addition of a small quantity of acetic acid, carbolic acid or orange juice. The juice from the leaves and stems of the *Costus Afer* and from the fruit of the *Papaya* (papaw) cannot be used for coagulation. The sap of the "mwengere" plant *(Cissus adenocaulis),* often used by the natives for coagulating the latex, seems to have a deleterious effect on the quality of the rubber.[389]

Whenever the most uniform product is desired, it is recommended that these natural materials be avoided (even though they may reduce tapping costs slightly) and only pure substances be used. In the case of these latter, the exact quantities for most satisfactory coagulation are easily determined.

Among organic acids, acetic acid, as in the case of *Hevea,* has been the one most extensively used. It accomplishes a good coagulation when used in the form of a 2 to 3 per cent solution. Formic acid functions at a smaller concentration, whereas citric and lactic acids must be used at higher concentrations. Tannin yields a more pasty product, which is difficult to remove from the tree.[390]

The coagulating material marketed by the firm of Lehmann and Voss under the name of "Coalatex," which material apparently consists primarily of oxalic acid and oxalates, gives a good coagulation at a concentration of 10 per cent.[391]

In the field of inorganic acids, hydrochloric and sulfuric acids bring about good coagulation of the latex when employed at a concentration of about 2 per cent. They are not given consideration for practical use, however, since they exert such a harmful effect on the bark of the tree. The high price of hydrofluoric acid (Purub), which coagulates latex at a concentration of 1 per cent, has prevented its adoption.

Calcium chloride, first recommended by the writer of this section,[392] is so low in price that it has been used extensively in German East Africa. It coagulates the latex satisfactorily at a concentration of 2 to 3 per cent. Mixtures of calcium chloride and acetic or carbolic acid were also much used for coagulation. Th. Marx [393] has proved that any significant lowering in cost cannot be accomplished with these mixtures, however.

It is stated by Marx [394] that sea water alone is not to be used for coagulation, although it becomes a good tapping agent after the addition of acetic acid (1 per cent), phenol (1 per cent), a mixture of acetic acid (0.15 per cent) and phenol (0.3 per cent), calcium chloride (1 per cent) or "Mbuyudekokt" (4 per cent).

With barium chloride, magnesium chloride, and magnesium sulfate, the writer obtained a less intensive coagulating effect than with calcium chloride. That magnesium sulfate is not to be used as a coagulant in the Lewa method was established by Th. Marx.[395] On the other hand, this same investigator [396] obtained good coagulation with magnesium chloride (5 per cent), calcium phosphate (5 per cent), superphosphate (3 per cent), ammonium sulfate (3 per cent), and zinc sulfate (1 per cent). Substances found to give no coagulation include sodium sulfate (2 and 5 per cent), sodium bisulfite (1.5 and

[388] *Pflanzer,* **5,** 19 (1909); **3,** 275 (1907).
[389] See Zimmermann, A., "Der Manihot-Kautschuk. Seine Kultur, Gewinnung and Präparation," p. 186. G. Fischer, Jena, **1913;** and Marx, Th. and Zimmermann, A., *Tropenpflanzer,* **25,** 36 (1922).
[390] See Zimmermann, A., "Manihot-Kautschuk," p. 310, G. Fischer, Jena, **1913.**
[391] See *Pflanzer,* **3,** 149 (1907).
[392] Zimmermann, A., *Pflanzer,* **7,** 499 (1911).
[393] *Pflanzer,* **10,** 152 (1914).
[394] *Tropenpflanzer,* **24,** 74 (1921).
[395] *Pflanzer,* **10,** 152 (1914).
[396] *Tropenpflanzer,* **24,** 79 (1921).

2.5 per cent), sodium thiosulfate (1 to 4 per cent), sodium sulfite (3 per cent), and primary sodium phosphate (1.5 and 3 per cent). Very weak and incomplete coagulation was given by potassium chloride (2 and 4 per cent), sodium borate (2 per cent), kainite (3 and 6 per cent), alum (1 to 4 per cent), aluminum sulfate (1 to 4 per cent) and boric acid (1 and 2 per cent). Furthermore, A. Zimmermann [397] obtained unfavorable results with potassium ferrocyanide (5 per cent), potassium dichromate (6 per cent), mercuric chloride (1 and 5 per cent), sodium chloride (2 and 5 per cent) and sodium fluoride (5 per cent).

Extensive use was also made of carbolic acid (phenol), which gives good coagulation when used at a concentration of 2 per cent. According to C. Kinzelbach and A. Zimmermann,[398] acidifying the phenol provides a coagulating agent which is even cheaper. They found, for instance, that a solution containing 0.4 per cent phenol and 0.2 per cent acetic acid coagulated the latex just as rapidly as 2 per cent phenol or 2 per cent acetic acid alone. Lysol (3 per cent), cresol (2.5 to 2.8 per cent), creolin (3 per cent) and creosote (2 per cent) also gave good coagulation, while alcohol, formaldehyde and pyridine could not be used.[399]

The experiments of Th. Marx [400] proved aniline hydrochloride (1 and 2 per cent) and a mixture of carbolic acid (0.6 per cent) and formic acid (0.3 per cent) to be good coagulants. Little or no separation of rubber resulted from the use of aniline (1 and 2 per cent), wood vinegar (5 and 7.5 per cent), sodium acetate (2 and 4 per cent), aluminum acetate (2 and 4 per cent) and sodium cresolate (1.5 per cent).

Of the alkaline reagents tested by Th. Marx,[401] the following were found to be of no service: sodium bicarbonate (2 and 4 per cent), sodium carbonate (3 per cent), barium hydroxide (1 to 3 per cent), and a mixture of barium hydroxide (1 per cent) and barium chloride (1 per cent). On the other hand, calcium chloride in the dry state is suitable for coagulating. Better results were obtained with mixtures, such as calcium hydroxide (1.5 per cent) and calcium chloride (1 per cent), calcium hydroxide (2 per cent) and calcium chloride (0.3 per cent), or calcium hydroxide (2 per cent) and carbolic acid (0.3 per cent).

In German East Africa, the rubber, after being collected from the trees while still damp, rolled up in balls, and laid out to dry for some time, was then put on the market in the form of these balls. In consequence of the high content of water and of proteins, decomposition phenomena took place readily. Although the properties of the rubber were not greatly influenced thereby, the highly unpleasant odor developed caused this rubber to be given a lower evaluation. Furthermore, in the Lewa method, it was not possible to avoid the inclusion of certain impurities, such as bark and earth, in the rubber. This fact led later to the adoption of methods of purification in the field. This purification was handled in part in large establishments provided with washing mills similar to those used in the preparation of Hevea rubber. To some extent use was also made of a simpler process, involving cutting the balls into slices and pressing these out between even speed rolls under a stream of water for some time. In certain cases these slices were subsequently soaked in pure water or water containing Purub (hydrofluoric acid). Up to the beginning of the World War, the methods used for the preparation

[397] *Pflanzer*, **1**, 310 (1905); **3**, 350 (1907).
[398] *Pflanzer*, **5**, 26 (1909).
[399] See Zimmermann, A., "Manihot-Kautschuk," p. 190, G. Fischer, Jena, **1913**.
[400] *Tropenpflanzer*, **24**, 75 (1921).
[401] *Tropenpflanzer*, **24**, 81 (1921).

of this rubber were still anything but uniform, and it was not possible to state with any assurance that one method yielded rubber better suited for commercial purposes than another. As with Hevea rubber, a definite standard method could not have been recommended. The carefully prepared uniform rubber could be readily sold, and brought a very good price.

Methods Involving Handling of the Latex

In preparing the different kinds of Manihot rubber from latex which has been collected in liquid form, several different methods apparently have been used, especially in Brazil. According to L. F. d'Almeida,[402] the smoking method, such as is used with Hevea, is often employed. E. Ule [403] states that formalin can be used as coagulant. A mixture of carbolic and sulfuric acid is recommended by A. Moulay.[404] According to O. Labroy and V. Cayla,[405] good rubber can also be obtained by spontaneous coagulation, which occurs rapidly upon dilution of the latex with 3 to 4 volumes of water. After about 10 hours, the coagulum takes on a consistency suitable for further handling.

C. de Mello Geraldes [406] states that in Angola the latex is allowed to coagulate spontaneously in shallow pans, either without dilution or after dilution with an equal volume of water. The subsequent handling is the same as with Hevea sheets. The use of smoke during the drying process is also quite common.

J. G. Smith and Q. Q. Bradford [407] recommend that the latex of *Manihot Glaziovii,* after previous neutralization, be allowed to stand 1/2 hour before the introduction of a boiling solution of ammonium sulfate. The whole is then warmed gently (not over 77° C.). As has been demonstrated by J. Parkin,[408] the latex can also be coagulated by boiling.

E. Marckwald and F. Frank [409] recommend the addition of magnesium salts or calcium phosphate in the case of coagulation with citric or acetic acid. When this method is used the final product is said to be superior in nerve and "body" to the usual rubber.

Ficus

Relatively large quantities of latex are seldom collected from *Ficus elastica* trees. Such latex cannot easily be coagulated by boiling, according to P. J. Burgess. This author recommends heating the latex to 40° C., adding a 2 per cent solution of tannin (10 per cent of the volume of the latex), and shaking. A. Preyer [410] states that good coagulation is obtained by pouring the latex into a boiling solution of chloral hydrate or formic acid. The recommendation of G. Mann [411] is to mix the latex with 2 per cent of formalin and allow it to stand in split bamboo rods protected from the sun. Coagulation will set in at the end of one day.

According to O. de Vries and W. Spoon,[412] the latex from *Ficus elastica* can be coagulated with acetic acid, provided some Hevea latex has first been added to the Ficus. Latex having a comparatively high rubber content can be coagulated by agitation (churning).

[402] d'Almeida, L. F., "De l'exploitation du caoutchouc au Brésil.," p. 21, Brussels, **1900.**
[403] *Tropenpflanzer,* **16,** 92 (1912).
[404] *L'agr. prat.,* **5,** 374 (1905).
[405] Labroy, O. and Cayla, V., "Culture et exploitation du caoutchouc au Brésil.," p. 188, Paris, **1913.**
[406] de Mello Geraldes, C., "Contribution pour l'étude des plantations des caoutchoutiers à Angola," Lisbon, **1914.**
[407] *Hawaii Agr. Exp. Sta. Bull.,* **No. 16.**
[408] *Roy. Botan. Gard. Ceylon, Circ.,* **1,** 145 (1899).
[409] *Gummi-Ztg.,* **26,** 1666 (1912).
[410] *Tropenpflanzer,* **4,** 327 (1899).
[411] *Agr. J. India,* **2,** 279 (1907).
[412] *Arch. Rubbercultuur,* **12,** 21 (1928).

P. van Romburgh [413] states that the latex from *Ficus Vogelii* is not coagulated by acetic acid, sodium chloride, or alum, nor by heating alone, but is coagulated by alcohol or by heating after the addition of acetic acid or hydrochloric acid. The latex can also be allowed to dry on the bark, and the dried portions can then be wound up. In western Africa the latex is said to be coagulated by heating with lemon juice. According to D. Spence,[414] the latex of *Ficus Vogelii* can be preserved by means of about 3 per cent of formalin.

R. Schlechter [415] states that the latex from *Ficus Schlechteri* can be easily coagulated by warming. This same author claims that such a method is also satisfactory for *Ficus hypophaea.*

A very peculiar method of coagulation, which was used with one of the species of *Ficus*, is described in the "Amtsblatt für das Schutzgebiet Togo." In this method,[416] a "dumpling" is first made from corn meal. The wound on the stem is rubbed or dabbed with the dumpling. The exuded latex is soaked up by the dumpling, the volume of the latter being considerably increased in the process. In order to remove the corn meal, the lump is finally kneaded vigorously under a stream of water.

Castilloa (Castilla)

In Brazil, Castilloa latex is usually coagulated by means of soap, according to O. Labroy and V. Cayla.[417] The soap is triturated and mixed with water, and then added to the latex to the extent of 25 grams per liter. With good agitation, there soon forms a more or less spongy mass, which can be stamped with the feet (while in a tank, for instance) to remove the serum. The mass is simultaneously opened up by means of a sharp-edged instrument. The rubber thus obtained is dried in the shade and put on the market under the name of "bolacha." In many districts, the latex is merely placed in pits or holes and allowed to evaporate. The very impure rubber obtained is designated as "pranchas." The rubber dried on the bark, which rubber is known as "sernamby," is that most highly valued.

The sap from the *Ipomoea bona nox* is also frequently used for coagulation. According to T. F. Koschny,[418] about one good handful of the plant, from which the leaves have been removed, is beaten to pieces on a stone or a piece of wood and is then mixed thoroughly with about 2 liters of water. The liquid which is pressed out is thoroughly stirred with 23 to 27 liters of latex. After a short time the latex curdles to a plastic mass, which is drawn several times through a small hand roller mill (wringer). The thin discs formed are finally hung in the shade to dry.

G. Waldrom [419] recommends the use of smoke for coagulation. Steam, carrying with it the smoke from a wood or nut fire, is introduced into the latex. After the latter has been brought to the boiling point, there are obtained spongy clumps of rubber, which are sufficiently porous to dry easily. They are also protected against decomposition, probably as a consequence of the preservative action of the smoke constituents.

[413] Van Romburgh, P., "Les plantes à caoutchouc et à gutta-percha," p. 112, Batavia, **1903.**
[414] *Gummi-Ztg.*, **22,** 956 (1908).
[415] *Tropenpflanzer*, **7,** 526 (1903).
[416] *Amtsblatt für das Schutzgebiet Togo*, **3,** No. 6 (1906).
[417] Labroy, O. and Cayla, V., "Culture et exploitation du caoutchouc au Brésil," p. 215, Paris, **1913.**
[418] *Tropenpflanzer Beihefte*, **5,** 154 (1901).
[419] *India Rubber World*, **36,** 188 (1906).

According to O. F. Cook,[420] attempts were made on the Zacaulpa plantation to produce rubber from Castilloa latex by a method the same as used for Para rubber. Only a sticky mass was obtained.

For the preparation of clean, light-colored rubber, C. O. Weber [421] proposed a method based on the fact that Castilloa latex creams, either in the diluted or undiluted condition. In this method, six times its volume of boiling water and then 30 cc. of commercial 40 per cent formaldehyde solution (formalin) are added to each kilogram of latex, in order to prevent the precipitation of proteins. The latex is then filtered through a fine-mesh gauze into a drum provided with a stopcock. This receptacle is filled to the top, covered, and allowed to stand. On the following morning, the lower layer of water is allowed to flow out through the stopcock. Separation is easy, since the rubber cream is too viscous to flow at this stage. The cream can either first be washed with cold water, or else the rubber particles can be made to agglomerate immediately by means of vigorous agitation. In the latter case, the resulting product is subsequently washed in the manner usual for fresh rubber. The freshly coalesced rubber forms sheets which at first feel peculiarly soft and flabby. Upon continued washing, a marked change in the rubber suddenly takes place. Within a few seconds, the sheet seems to contract and to become very tough and elastic. This change is evidenced by the fact that the sheet begins to crackle on the mill.

R. H. Biffen [422] states that by centrifuging it is easy to remove the rubber from the latex completely. At a speed of 6000 r. p. m., only 3 to 4 minutes were required. This same writer [423] states that the mass obtained can be once more dispersed, and, after redispersion, can no longer be coagulated by ammonia.

O. Labroy and V. Cayla [424] report that in Trinidad a machine capable of producing a good light-colored rubber by a centrifuging process was put in operation. According to C. Beadle and H. P. Stevens,[425] the cream formed by centrifuging the latex tends to leave a white coating adhering to the fabric on the inner walls of the centrifuge. If this layer, which has a water content of about 17.4 per cent, is not touched by the fingers, it dries quickly, a layer 6 mm. thick being completely dried in a few hours. On the other hand, if the layer is pressed lightly with the fingers, 2 to 3 weeks are required to complete the drying.

Contradictory statements regarding the effect of acids and alkalies on Castilloa latex are to be found in the literature. The discrepancies may perhaps be partly explained by the fact that different authors have used latices from different species.

According to C. O. Weber,[426] the careful addition of acids to the latex (which itself exhibits a distinctly acid reaction in the fresh condition) leads to more or less rapid coagulation. Subsequent heating makes the coagulation especially rapid. When added in larger quantities, acids do not bring about coagulation, even after continued boiling. The strength of the acid does not seem to be the determining factor in the coagulation process, since tannin is far superior to hydrochloric acid, and acetic acid is just as good as hydrochloric.

[420] *U. S. Dept. Agr. Bur. Plant Ind., Bull.*, **49**, 72 (1903).
[421] Reprint from *Gummi-Ztg.*, **17**, 34 (1902).
[422] *Kew Bull. Misc. Information*, 179 (1898).
[423] *Ann. Botany*, **12**, 165 (1898).
[424] Labroy, O. and Cayla, V., "Culture et exploitation du caoutchouc au Brésil," p. 219, Paris, **1913**.
[425] *Kolloid-Z.*, **13**, 210 (1913).
[426] Reprint from *Gummi-Ztg.*, **17**, 39 (1902).

On the other hand, both P. van Romburgh [427] and R. H. Biffen [428] report that Castilloa latex cannot be coagulated with acids. This statement has also been confirmed by A. W. K. de Jong and W. R. Tromp de Haas,[429] particularly for hydrochloric and tannic acids. They state that acetic acid in excess will always bring about complete coagulation, however.

The behavior of Castilloa latex toward alkalies is the same as toward acids, according to C. O. Weber.[430] The addition of ammonia in small quantities results in the production of an intense yellow-green color and coagulation. When used in excess, no coagulation takes place. Caustic soda has the same effect as ammonia, but brings about an even more intensive coloration. Van Romburgh,[427] de Jong and Tromp de Haas,[429] and J. Parkin [431] observed no separation of rubber upon the addition of alkalies.

Ferric chloride, mercuric nitrate, and ferrocyanic acid have been mentioned as good coagulants by C. O. Weber.[432] According to P. Olsson Seffer,[433] the coagulation of Castilloa latex is promoted by the vapors of burning sulfur. The addition of sulfur to the latex is said to preserve it against decomposition.

Separation of the rubber in this latex may be brought about by the addition of ethyl and methyl alcohols, according to the opinions of van Romburgh,[427] of Weber,[432] and of de Jong and Tromp de Haas.[429] As was demonstrated by van Romburgh, not all of the proteins are removed in this coagulation. Whereas the fresh latex contains 0.36 per cent of nitrogen, there is but 0.2 per cent in rubber which has been coagulated by means of alcohol. De Jong and Tromp de Haas observed further that, up to a certain optimum addition, the quantity of rubber obtained increases with the amount of alcohol added; beyond this optimum further addition of alcohol leads to a decrease in yield. C. O. Weber's [434] explanation of this observation was that the rubber, which is not yet completely polymerized, is soluble in concentrated alcohol.

It is reported by Weber [435] that acetone coagulates Castilloa latex. When the addition of acetone exceeds a certain optimum there is a diminution in the quantity of rubber separated, according to de Jong and Tromp de Haas.[436] Weber has contributed the further information that formaldehyde does not coagulate the latex, even when the latter is warmed. Furthermore, he [437] agrees with de Jong and Tromp de Haas in reporting that boiling is not effective in producing coagulation. Weber observed, moreover, that the latex was changed by warming into a liquid which was free from clots and from which the rubber cream separated slowly and incompletely on standing.

It is stated by R. Guerin [438] that the latex can be kept indefinitely in a cool place without the occurrence of coagulation.

Kickxia

The natives of Lagos allow the latex of *Kickxia clastica* to stand covered with palm leaves for 12 to 14 days, according to R. Henriques.[439] The coagulated rubber is then kneaded, pressed, and marketed in the form of

[427] van Romburgh, P., "Les plantes à caoutchouc et à gutta-percha," p. 79, Batavia, **1903.**
[428] *Kew Bull. Misc. Information*, 177 (1898).
[429] *Ber.*, **37,** 3299 (1904).
[430] *Ber.*, **36,** 3103 (1903).
[431] *Ann. Botan. Gard. Ceylon, Circ.*, **1,** 154 (1899).
[432] *Ber.*, **36,** 3103 (1903).
[433] *Gummi-Ztg.*, **22,** 636 (1908).
[434] *Gummi-Ztg.*, **19,** 103 (1904).
[435] *Ber.*, **36,** 3110 (1903).
[436] *Ibid.*, **37,** 3299 (1904).
[437] Reprint from *Gummi-Ztg.*, **17,** 29 (1902).
[438] *J. d'Agric. Trop.*, 73 (1902).
[439] Henriques, R., "Der Kautschuk und seine Quellen," p. 218, Dresden, **1899.**

balls. It is recommended by R. Schlechter [440] that the latex be boiled in pots of some kind with constant agitation, after the preliminary addition of three or four volumes of water. C. Christy [441] states that better results are obtained by an addition of tannin or sublimate, especially if the latex has previously been allowed to stand for ten days. With fresh latex, coagulation is not possible unless some acetic acid is first added; without acetic acid there is need for the addition of formaldehyde directly to the fresh undiluted latex. Good results were also obtained by pouring latex, to which some Purub (hydrofluoric acid) had been added, into boiling water. Coagulation of Kickxia latex is also said to be accomplished by the addition of latex from various species of *Strophanthus*.

Schulte [442] recommends a method of preparation, the first step in which is to pour one liter of latex into a pan, 40 cm. long, 30 cm. wide and 10 cm. deep. About 75 cc. of a 20 per cent solution of tannic acid are then added, with constant agitation. After about 2 minutes, the latex is coagulated sufficiently so that the cakes of coagulum can be moved around with the hands; after one more minute, it is completely coagulated. As soon as possible, the cakes are pressed into a sheet between ribbed rolls. The sheets are then allowed to lie for some time in water (preferably flowing) and are finally dried in the usual manner.

The recommendation of H. Bücher [443] is to pour the previously strained latex in a thin layer on a smoothly planed board, made of soft absorbent wood and provided with a peripheral ledge about 2 cm. high. After being allowed to dry in the shade, the rubber is pulled away from the board and rolled up.

Kickxia latex is coagulated by formaldehyde, according to P. Schidrowitz.[444] The rubber thus obtained is said to be characterized by an unusual toughness. P. Schidrowitz and F. Kaye [445] report that acetone coagulates Kickxia latex. The resulting coagulum has approximately the same resin content as when other methods of coagulation are used.

It has been stated by F. Eduardoff [446] that a 2 per cent solution of cresol, when added in a quantity four times that of the latex, brings about a good coagulation after shaking. On the other hand, crude carbolic acid (2 per cent) and acetic acid (2 per cent and concentrated) accomplish no coagulation, and 98 per cent alcohol and a 2 per cent Coalatex solution (*see* p. 129) only very slow coagulation.

Undiluted Kickxia latex withstands coagulation for a long time, according to P. Schidrowitz and F. Kaye.[447] Only 12 per cent of the rubber in a sample of latex bottled in Africa was found to have been coagulated during transportation to England. When diluted with 5 volumes of water, the latex exhibited a tendency to cream during transportation. When such a substance as ammonium oxalate, calcium chloride or magnesium sulfate was also added to the latex, no creaming occurred. Calcium chloride did bring about flocculation when used in relatively large quantities. In this respect it differed from barium chloride. It was demonstrated by C. Kinzelbach and A. Zimmermann [448] that creaming occurs when the latex is diluted with 10 to

[440] Compare P. Reintgen, *Tropenpflanzer Beihefte*, **6**, 166 (1905).
[441] Christy, C., "The African Rubber Industry and Funtumia Elastica," p. 218, London, **1911**.
[442] *Tropenpflanzer*, **17**, 580 (1913).
[443] Reprint from *Dt. Kolonialbl.*, No. 12/13 (1910).
[444] Schidrowitz, P., "Rubber," 2nd ed., p. 128, Methuen & Co., London, **1916**.
[445] *India Rubber J.*, **34**, 377 (1907).
[446] *Gummi-Ztg.*, **22**, 387 (1908).
[447] *India Rubber J.*, **34**, 377 (1907).
[448] *Pflanzer*, **5**, 33 (1909).

20 times its volume of water. The rubber particles in the cream cannot be caused to unite by shaking nor by centrifuging, although they will stick together immediately after collection on a filter. When the liquids are separated from the rubber by filtration, the latter can be removed as a continuous sheet.

According to E. Fickendey,[449] warming the latex in an autoclave leads finally to the formation of a pasty mass, which becomes tough and elastic upon stirring in the cold. If the latex is allowed to freeze, the rubber coagulates, and the serum can be pressed out after thawing.

HANCORNIA

In Brazil the latex of *Hancornia speciosa* is heated in a shallow vessel, or treated with pulverized alum, according to Ule.[450] The consistency imparted to the latex by these treatments is such as to allow the formation of large clumps by a kneading process. The rubber obtained by the heating method is said to have the better quality. Hoff [451] states that a mixture of two parts of alum with one of sodium chloride may be employed, while van Dionant [452] describes the use of salt water, alum, or citric acid for the coagulation of the latex in sunlight.

MASCARENHASIA

It is reported by Jumelle [453] that the latex of *Mascarenhasia arborea* is either allowed to dry on the trunk of the tree, or, after collection, is coagulated by boiling. The natives permit the latex from *Mascarenhasia lisianthiflora* to dry on the tree.[454] This latex is a thick liquid, which is coagulated rapidly by alcohol but less readily by citric acid or sulfuric acid. A sticky product is said to result from the use of these acids as coagulants.

The writer [455] has observed that in eastern Africa the natives either allow the latex of *Mascarenhasia elastica* to dry on the tree or else spread it over their hands and arms. In the latter process, the latex is soon coagulated sufficiently so that the rubber can be rolled up. The Lewa method of treating the wounds on the trees with lemon juice, acetic acid, carbolic acid, or Coalatex, does not give satisfactory results with this latex.

LIANAS (VINES)

In the cases of the African rubber-containing vines, which belong almost exclusively to the *Landolphia* or *Clitandra* genera, the natives often allow the latex to flow out on the bark to dry. E. de Wildeman and L. Gentil [456] state that the rubber from a morning's tapping can be collected in the afternoon or the next morning. It is rolled into small rods, known as "spindles," or may be united into "balls." At times, the rubber is cut into cubes or irregularly shaped pieces, which are designated as "thimbles."

The coagulation is often accelerated by rubbing certain plant juices or chemicals on the bark before tapping, or by sprinkling them on after the latex has been exuded. In the case of *Landolphia Heudelotii,* Jumelle [457] reports that lemon juice or a solution of sodium chloride is used. These same

[449] *K. W. Z.*, **8**, 45 (1911).
[450] *Tropenpflanzer Beihefte*, **6**, 28 (1905).
[451] *Kol. Kult. Colonies*, **4**, 88 (1899).
[452] *Gummi-Ztg.*, **22**, 825 (1908).
[453] "Rubber Recueil," 38.
[454] Jumelle, H., "Les plantes à caoutchouc et à gutta," p. 366, Paris, **1903.**
[455] *Pflanzer*, **3**, 146 (1907).
[456] de Wildeman, E. and Gentil, L., "Lianes caoutchoutifères de l'État Indépendant du Congo," p. 151, Brussels, **1904.**
[457] Jumelle, H., "Les plantes à caoutchouc et à gutta," p. 297, Paris, **1903.**

agents are employed with *Landolphia owariensis*. The writer has also observed the use of these coagulants with *Landolphia Kirkii*. In many districts, sea water also serves the purpose with this latter species.

The practice of hastening coagulation by spreading the latex over the arms or the uncovered breast is followed by the natives to some extent (in Pemba, for instance).[458] The coagulation is probably brought about by the heat of the body, assisted possibly by the chemical reaction of the perspiration.

After collection, the latex of *Clitandra orientalis* or of *Cl. nzunda* is coagulated by heating or by pouring into boiling water, according to E. de Wildeman and L. Gentil.[459] The same methods are also used with *Parameria glandulifera* and *Xylinabaria Reynaudi*.[460]

The coagulation can also be accelerated by the addition of certain reagents, such as acidic extracts from plants. In western Africa, the juice of the so-called "Bossanga" plant (*Costus Lukasianus* and other species of *Costus*) is much used. This juice or sap is obtained by merely twisting the stalks. According to Jumelle,[461] use is also made of the juice from the fruit of the "Baobab" (*Adansonia digitata*). An extract is obtained by macerating the pulp in water. Among coagulating agents, Jumelle also mentions the leaves of the *Bauhinia reticulata* and the *Hibiscus Sabdariffa* plants, and the fruit of the *Tamarindus indicus*.

According to A. Chevalier,[462] the latex of *Clitandra elastica* is difficult to coagulate. The recommended procedure is to boil the diluted latex for a long time, and to knead together by hand the rubber which has become separated but not agglomerated.

Jumelle[463] is the authority for the statement that the best rubber is obtained by allowing the latex to ferment spontaneously, in the case of *Landolphia Perrieri*. Acids and various salts can also be used satisfactorily as coagulating agents. Alcohol is a poor coagulant. Upon boiling the latex, separation of rubber takes place only in accordance with the percentage of water evaporated. The rubber obtained is said to be of inferior quality.

According to Jumelle,[464] a 5 per cent solution of sulfuric acid is generally used as a coagulant for the latex of *Landolphia sphaerocarpa*. Rubber of less value is obtained by coagulation with salt or by means of boiling.

Jumelle[465] states, furthermore, that the latex of *Cryptostegia madagascariensis* cannot be brought to coagulation by means of sodium chloride. It is also difficult to coagulate with acids. The experiments of the writer[466] indicate that acetic acid, carbolic acid, lemon juice, sodium chloride and Coalatex are all ineffective as coagulants, when applied to the bark of the *Cryptostegia grandiflora* tree.

Lemon juice, tamarind juice, and sodium chloride are used in coagulating the heated latex of *Marsdenia verrucosa*, according to Jumelle.[467] E. de Wildeman[468] reports that the latex of *Periploca canescens* can also be coagulated by heating it with lemon juice.

It is reported that the coagulation of the latex of *Landolphia Dawei* is brought about in Uganda by means of sodium chloride. The coagulum obtained is pressed between rollers.

[458] See *Rev. cult. coloniales*, **10**, 167 (1902).
[459] de Wildeman, E. and Gentil, L., "Lianes caoutchoutifères de l'État Indépendant du Congo," pp. 32 and 83, Brussels, **1904**.
[460] See Jumelle, H., "Les plantes à caoutchouc et à gutta," pp. 418 and 430, Paris, **1903**.
[461] *Ibid.*, p. 37.
[462] *L'agr. prat.*, **3**, 64 (1903).
[463] Jumelle, H., "Les plantes à caoutchouc et à gutta," p. 335, Paris, **1903**.
[464] *Ibid.*, p. 340.
[465] *Ibid.*, p. 264.
[466] Zimmermann, A., *Pflanzer*, **3**, 148 (1907).
[467] *Rev. cult. coloniales*, **10**, 93 (1902).
[468] *J. d'agric. trop.*, **5**, 347 (1905).

The rubber in the latex of *Landolphia Heudelotii* may be isolated by centrifuging, according to H. Hamet.[469]

Euphorbia

The investigations carried out by A. Zimmermann [470] indicate that the latex of *Euphorbia tirucalli* is coagulated neither by boiling nor by treatment with such agents as acetic acid (5 per cent), tartaric acid, dilute hydrochloric or sulphuric acid, formaldehyde, alum, calcium chloride or ammonium carbonate. Moreover, a coagulum suitable for further working was not obtained by using carbolic acid, sublimate, caustic soda, ammonia, or common salt. Although good coagulation resulted from the use of alcohol, the best of all was obtained with tannin. When a one or two per cent solution of tannin was added to the undiluted latex, the latter congealed within a short time to form an apparently homogeneous mass. The rubber present could then be readily pressed into a ball by hand. When the latex was poured into the tannin solution, less favorable results were obtained. For the coagulation of this latex, Noyes [471] recommends a mixture of tannin and hydrochloric acid. The coagulation is said to progress more satisfactorily if the latex is first allowed to stand from one to seven days, and is then heated to about 60° C. after the addition of the reagents.

The latex of *Euphorbia angularis* behaves in essentially the same way towards the above-mentioned reagents as does that of *Euphorbia tirucalli*. It is coagulated by a solution of tannin, a sticky viscous mass being formed. This mass can be kneaded and pressed with the hands, provided they have been previously moistened to prevent them from sticking fast to the rubber. If the mass, after being pressed, is placed on a moistened glass plate, it spreads out over the latter rapidly. A solid crust is gradually formed on the surface of the rubber. Whether this occurs solely as a consequence of drying, or is associated with oxidation phenomena, has not been determined.

The latex of *Euphorbia Reinhardtii* becomes solid within a short time, without the addition of any coagulating agent.

For the coagulation of the latex of *Euphorbia tirucalli* a mixture of hydrochloric and tannic acids is recommended by E. Neufeld.[472] The latices from *Euphorbia grandidens*, *E. tetragona* and *E. triangularis* plants readily undergo spontaneous coagulation. If it is desired to maintain these latices in a liquid condition, ammonia, formalin, boric acid, *beta*-naphthol, or a casein soap solution is added. Fluorides or paranitrophenol can also be added as antiseptics. The addition of ammonia, and the simultaneous dilution of the latex with an equal volume of water, has proved to be the most desirable procedure.

Jelutong

Jelutong, which is derived particularly from the various species of *Dyera*, and which is used extensively in the manufacture of chewing gum, is frequently lowered in value either by being darkened in color by a fungus or by being disintegrated into a powdery mass. It is said that both of these possibilities can be avoided by making use of the method of coagulation

[469] *L'agr. prat.*, **1**, 23 (1901).
[470] *Pflanzer*, **7**, 742 (1911).
[471] *J. Union South Africa*, 706 (1913).
[472] *Kautschuk*, **3**, 361 (1927).

proposed by B. J. Eaton, C. D. V. Georgi, and G. L. Teik.[473] The first step in this process is to remove the impurities by passing the latex through a fine metal screen. To each three gallons of latex in a 4-gallon petroleum can is then added 0.5 fluid ounce of a 10 per cent solution of acetic acid. The loosely covered can is heated, with constant stirring of the contents, and the latex is allowed to boil for about three minutes. The coagulum obtained in this manner is placed on a bamboo screen, pressed well, and then boiled for 10 minutes in a large iron pan (filled with water). The coagulum is turned over frequently during the boiling, and is then pressed with a board. The final compression is carried out in a block press, the inside dimensions of which are about 12 x 5 x 5 inches. The resulting block is then washed with water and dried. The blocks are preserved under water until ready to be transported.

Sodium silicofluoride also gives a satisfactory coagulum. The toxicity of this material prevents it from being considered as a coagulant for jelutong which is to be used for the preparation of chewing gum.

Guttas

Since gutta-percha* and balata are used in the rubber industry, and since both of these materials have an empirical formula the same as that of rubber, $(C_5H_8)_x$, it does not seem amiss to mention the methods of preparation used with these guttas.

In the case of gutta-percha, the treatment of the latex varies somewhat with the species from which it is obtained. In the early days the custom was to fell the trees of certain species (*Pallaquium*, for instance) and collect the latex by making cuts around the trunk at intervals of 12 to 18 inches.[474] In this method, the latex coagulates in the cuts and the coagula are scraped off with a knife. After the mass of crude material is freed from impurities by boiling in water, it is rolled into sheets. These sheets become hard upon cooling, and are then ready for shipment. At the present time extraction methods,[475] in which the gutta is obtained by extracting the leaves, are coming more and more into vogue. Tapping is also practiced to some extent. Latex from trees of the *Payena* species, which can be tapped more satisfactorily than can the *Pallaquium* species, should be collected not later than one hour after sunrise, as otherwise an objectionable discoloration develops. This latex is coagulated by boiling. The resulting crude gutta is cut into pieces, softened in hot water, washed in a washing machine, forced through a strainer, washed again, worked in a kneading machine, and finally sheeted out in 5-foot slabs, varying from one-eighth to one-fourth inch in thickness. Commercial gutta-percha contains from 10 to 60 per cent of resin, consisting of albane, a crystalline resin, and flauvile, a yellow amorphous resin, in the ratio of about 2 to 1.

Balata is obtained from certain species of *Mimusops*, which are to be found in Trinidad, the Guianas, Venezuela, and adjacent regions.[476] To facilitate collection of the latex, the trees were formerly felled. This practice was followed in Venezuela until recently. In British and Dutch Guiana, on the other hand, the trees are always tapped. The latex is allowed to ferment for two or three days, after which time the upper layer coagulates. The coagulated layer is removed and dried after it has attained a thickness of about 0.6 cm. The attempts to make use of extraction methods such as those used with gutta-percha have not been very successful. Commercial balata is softer than gutta-percha, as it contains more of the softer resin, flauvile. The ratio of albane to flauvile in the resin of balata is about 2 to 3.

The reader who desires to consult a more thorough treatise on these materials is referred to Emil J. Fischer's recent book, "Guttapercha und Balata," Allgemeiner Industrie-Verlag, Berlin-Lichterfelde, **1933**.

[473] *Malayan Agr. J.*, **14**, 275 (1926); **15**, 65, 400 (1927).

* Translator's note by V.N.M.

[474] See Hauser, E. A., "Latex," (English translation by W. J. Kelly), pp. 49-51, Chemical Catalog Co., Inc., New York, **1930**; and *Bur.* [illegible] **20**, Allgemeiner Indu[illegible]

[476] See Hauser, *loc. cit.*

Differences in the Quality of Rubber from the Same Species

Individual Fluctuations Within the Same Species

Since the *Hevea* trees of the Middle East did not all originate from the same stock, variations between individual trees with respect not only to yield capacity (see p. 42), but also to the chemical composition of the latex and the physical properties of the products obtainable, are to be expected. Such variations have been observed, particularly in the case of the rubber content of latices from trees which are of the same age, which have been exposed to the same soil and climatic conditions, and which have been tapped alike. Moreover, it has been proved by G. S. Whitby [477] that no correlation exists between the yield and the rubber content of a given latex. The color of the latex, which is almost pure white with most trees, has been observed to be a more or less intense orange-yellow in the case of certain trees. Moreover, the violet coloration which the rubber exhibits upon being brought in contact with the air (see p. 101) is of quite different intensity with different trees, even though they may have been subjected to the same conditions. Such variations are to be attributed to the peculiarities of individual trees, which peculiarities are transmitted by vegetative propagation.

It was proved by O. de Vries [478] that, although the rate of vulcanization is approximately constant for rubber obtained from the same tree under different conditions, it may vary greatly in the case of rubbers obtained under the same conditions from different trees of the same species. Although conspicuous deviations may be observed between the tensile strengths of the vulcanizates and the viscosities of the solutions of rubbers from different trees, the corresponding extensibilities show only small variations.

Influence of the Age of the Plant (or of the Part of the Plant Being Tapped)

The investigations of O. de Vries [479] led him to conclude that the rubber from trees from three to four and one-half years old is characterized by a decided "shortness." In general, the physical properties of such rubber were found to be low. When R. Riebl [480] investigated the same trees about eight years later, he found the physical properties of the rubber obtained to be much improved, but not yet quite equivalent to those of normal Hevea rubber. In interpreting these observations, consideration must be given to the fact that the above-mentioned trees were grown at a relatively high altitude (600 meters above sea level). At this elevation the trees had developed rather slowly, so that the rubber content of the latex was less than that of trees grown in lower country. According to de Vries,[481] no constant differences between the physical properties or the chemical compositions of rubbers from 8-year old and from 30-year old trees have been discovered. C. Beadle and H. P. Stevens [482] reported that the acetone extract (7.12 per cent), the protein content (13.02 per cent) and the sugar content (2.25 per cent) of the rubber from a very young part of an *Hevea* tree (i. e., the leaf stems) were comparatively large.

[477] *India Rubber J.*, **58**, 895 (1919).
[478] de Vries, O., "Estate Rubber," p. 51, and *Arch. Rubbercultuur*, **4**, 249 (1920); **6**, 140 (1922). Also see *Rubber Res. Scheme Bull.*, **29** (1922).
[479] *Arch. Rubbercultuur*, **6**, 296 (1922).
[480] *Arch. Rubbercultuur*, **11**, 155 (1927).
[481] de Vries, O., "Estate Rubber," p. 53.
[482] *India Rubber J.*, **41**, 216 (1911).

Exact studies of the relationships between the rubbers obtained from young and from old *Manihot* trees do not appear to have been made. According to Y. Henry,[483] the rubber from four-year old trees is inferior. On the other hand, J. Parkin [484] states that good rubber is obtainable from young shoots. Moreover, the rubber obtained from two-year old trees in German East Africa seemed to have very good properties. In a sample obtained from a 13-month old tree, W. Schellmann [485] found the ratio of resins to pure rubber to be 12.1 to 100.

In the case of *Castilloa,* rubbers obtained from trees of different ages or from various parts of the same tree exhibit considerable variation in resin content. Thus C. O. Weber [486] found the resin in rubber from different parts of the same tree to vary as follows:

	Per Cent
From the trunk	2.61
From large branches	3.77
From branches of medium size	4.88
From young twigs	5.86
From leaves	7.50

As demonstrated by the figures shown below, Weber also found that the resin content of rubber from the trunks of the trees decreased with the age of the trees.

Age of trees Years	Resins Per cent	Age of trees Years	Resins Per cent
2	42.33	5	18.18
3	35.02	7	11.59
4	26.47	8	7.21

Similar results were obtained by the Imperial Institute [487] with samples originating in Trinidad. Calculated on the basis of dry, dirt-free rubber, the resin contents were as follows:

	Per cent
From 4-year old trees	65.6
From 4½-year old trees	52.6 - 56.6
From trees at least 12 years old	8.3 - 14.3

Upon investigating samples obtained from New Guinea, Fendler [488] reported furthermore:

Age of trees Years	Resins Per cent	Rubber Per cent
2	59.1	40.9
3	22.0	78.0
5	20.7	79.3

With other samples from New Guinea, Mannich [489] found the α rubber from 3½- and from 6-year old trees to be 58.6 and 84.0 per cent respectively, while the β rubber was 2.8 and 1.6 per cent respectively.*

[483] Henry, Y., "Le caoutchouc dans l'Afrique occidentale francaise," p. 95, Paris, **1906.**
[484] *Roy. Botan. Gard. Ceylon, Circ.,* **1,** 116 (1899).
[485] *Pflanzer,* **2,** 12 (1906).
[486] Weber, C. O., "Reise nach einer Kautschukplantage in Kolumbien," Dresden. Reprinted from *Gummi-Ztg.,* **17,** 72, 32 (1902).
[487] *Bull. Imp. Inst.,* 160 (1903).
[488] *Tropenpflanzer,* **8,** 140 (1904).
[489] *Ibid.,* **6,** 402 (1902).
* Translator's Note. The α and β terminology of Mannich is obviously different from that of Hauser and other recent investigators. —V. N. M.

Ficus elastica behaves like *Castilloa* with respect to resin content. Thus with samples from New Guinea, Fendler [490] found the resin content to vary with the age of the tree, as follows:

Age of trees, Years	Resin, Per cent
2	27.0
3	41.0
4	11.0
5	8.5

The values obtained by W. R. Tromp de Haas [491] at Buitenzorg were:

Age of trees, Years	Resin, Per cent
3	36.4
4	31.6
9	8.9

This same author [492] found the resin content of the rubber to vary with the distance of the tapping cut up the trunk of the tree. In the case of a 20-year old tree, he reported the following variation:

Distance above ground, Meters	Resin, Per cent
1.3	4.14
6	5.7
9	6.0
12	6.0
15	5.9

With samples from a 25-year old tree, he [493] found that the resin content of rubber from the trunk (at a height of 4 meters) was 4.9 to 6.1 per cent, from the older parts of the roots 8.4 to 8.6 per cent, and from the younger parts of the roots 23.7 to 24.2 per cent. Moreover, from the leaves and leaf stalks, A. Preyer [494] was able to obtain rubber which was elastic and not sticky.

In the case of certain of the rubber-producing vines, the quality of the rubber has likewise been found to vary considerably with the age of the plant. Thus J. Parkin [495] and J. Dybowsky [496] found that the rubber from young *Landolphia Heudelotti* plants was not only small in quantity but also low in quality. Furthermore, Parkin obtained good rubber from the older branches, but only a sticky substance from the young twigs of *Landolphia Kirkii*. The same observation was made by H. Jumelle and H. Perrier de la Bathie [497] in the case of *L. crassipes*, and by H. Jumelle [498] in the cases of *Landolphia trichostigma*, *Gonocrypta Grevii* and *Cryptostegia madagascariensis*. The last-mentioned investigator also obtained a sticky product from the younger branches and from the base of the stem of the *Landolphia mandrianambo* plant. At a certain height up the stem good rubber was usually obtained.

[490] *Tropenpflanzer.* **8,** 140 (1904).
[491] *Meded. Proefst. Buitenzorg,* Verslag voor het jaar, **1903,** 73 and **1904,** 51.
[492] *Ibid.,* **1903,** 72.
[493] *Ibid.,* **1904,** 51.
[494] *Tropenpflanzer.* **4,** 237 (1900).
[495] *Roy. Botan. Gard. Ceylon, Circ.,* **1,** 162 (1899).
[496] *L'agr. prat.,* **4,** 272 (1904).
[497] Jumelle, H., and Perrier de la Bathie, H., "Les Landolphia et les Mascarenhasia à caoutchouc du Nord de l'Andalava," p. 28, Paris, **1910.**
[498] "Rubber Recueil," 37 and 35, and "Les plantes à caoutchouc et à gutta," p. 264, Paris, **1903.**

Influence of the Season, Climate, Soil and the Treatment Given the Tree

Since the percentage of water in latex is greater in wet than in dry weather, it is apparent that the season of the year can exert an influence on the composition of the latex. On the other hand, any influence of the season on the properties of the rubber has not yet been established, according to O. de Vries.[499]

Changes in the composition of the latex usually take place during the time when the tree loses its leaves, or subsequently, while it is standing bare or forming new leaves and flowers. According to de Vries,[500] rubber obtained during this period frequently exhibits, after coagulation, a strong violet coloration. During this period, the percentage of quebrachitol in the latex may also sink from 2.0 to 0.5 per cent, and the reducing sugar may largely disappear. On the other hand, the properties of the rubber produced do not appear to deviate much from normal.

Other factors capable of affecting the total yield and also the water content of latex include the nature of the soil, the use of fertilizers, the care given the plants, and various diseases. Whether these factors also influence the properties of the rubber has never been determined with exactness.[501] Rubber differing little from normal was usually obtained by de Vries [502] from trees which had been topped and subsequently transplanted. The same author [503] also found that lack of care of the tree did not affect the properties of the rubber.

Influence of the Method of Tapping

The method of tapping used has considerable effect on the composition of the latex obtained.[504] The rubber content is high as a rule at the beginning of a tapping period. Upon continued tapping there is soon reached a state of equilibrium, characterized by the fact that the composition of the latex remains approximately constant, provided the external conditions are constant and the tree does not pass through the "wintering" period. In the case of abnormally heavy tapping, as was formerly the usual case upon plantations, the decrease in rubber content continues until a value of 16 per cent or less is reached. Under these conditions the protein content likewise decreases, but generally at a slower rate than the rubber content. The ratio of resinous materials to pure rubber appears to be independent of the tapping procedure. The carbohydrate and ash contents often seem to increase with heavy tapping, although they sometimes remain unchanged or even decrease.

If the trees are allowed to stand untapped for some time, the changes which occur in the composition of the latex are the reverse of those resulting from heavy tapping; i. e., the rubber and protein contents steadily increase. Latex of high rubber content is also obtained when, during tapping, the base of the trunk is reached and a beginning is made on a new tapping surface.

Properties especially affected by the method of tapping include the rate of vulcanization and the viscosity of the solution of the rubber. When tapping is moderate, these properties remain practically unchanged. With

[499] *Arch. Rubbercultuur*, **7**, 217 (1923).
[500] de Vries, O., "Estate Rubber," p. 49.
[501] de Vries, O., "Estate Rubber," pp. 47 and 70.
[502] *Mededeel. Centraal Rubbersta.*, **No. 37** (1923).
[503] *Arch. Rubbercultuur*, **6**, 289 (1922).
[504] Compare W. A. Arisz in *Mededeel. Besoekisch Proefsta. Rubberserie* **No. 13** (1920); **No. 24** (1927); and de Vries, O., "Estate Rubber," p. 62.

heavy tapping, more or less of an increase in the rate of vulcanization of the rubber and a decrease in the viscosity of its solution result. A pause in tapping leads to changes in the opposite direction. An unvarying relationship between the changes in the rate of vulcanization and in the viscosity does not seem to exist, however.[505]

The method of tapping seems to have no significant influence on the mechanical properties of the rubber after vulcanization.

In order to obtain rubber with the greatest possible uniformity it is advisable not only always to use the same method of tapping but also to distribute the dates for rest periods, for beginning on new tapping surfaces, and even for topping the trees, so that these changes will be occurring only on a small portion of the plantation at any given time. Although the adverse effect of the "wintering" of the tree on the uniformity of the rubber cannot be avoided, the practical effect of this factor is decreased by the fact that "wintering" occurs at different times for the individual trees on a plantation. A certain equalization is thus brought about by the trees themselves.

Influence of Methods of Preparation and Storage on the Appearance and Properties of Rubber

Variations in the Appearance of Crude Rubber

Although appearance does not play the part in the evaluation of crude rubber that it formerly did, some importance is still attached to a uniform appearance, especially in the case of the more valuable commercial grades. In the preparation of plantation rubber, the constant endeavor is therefore to produce rubber of normal appearance. Below is presented a discussion of the various observed deviations from normal appearance, which deviations are sometimes accompanied by a lowering of the properties of the rubber.

Presence of Air Bubbles

Air bubbles can easily be introduced into rubber (especially sheets) at the time the latex is being poured into the mixing tank and diluted, or when the coagulating agent is being added, provided the subsequent coagulation is too rapid for the bubbles to escape. This defect, which is primarily one involving only the external appearance of the sheets, can readily be avoided by making the coagulation process slower and by carefully removing all foam before coagulation.

Decompositions occurring during coagulation (maturation—*see* p. 102) can also result in the formation of gas bubbles. The presence of such bubbles can be prevented by the use of anti-coagulants, by more rapid working of the coagula, and by faster drying.

It is reported by J. C. Hartjens [506] that air bubbles of the size of a pea or larger can be produced on the upper surface of suspended sheets, when the roof of the drying house is too strongly heated by the sun. By so protecting the roof that the temperature of the drying house never reaches 70° C., this defect may be avoided.

[505] See de Vries, *Arch. Rubbercultuur*, **2**, 437; **4**, 313 (1920).

[506] *Mededeel. Proefsta. Malang.*, **27**, 12 (1919).

Dark Coloration of Rubber

In the case of Hevea, darkening of the rubber results largely from the previously described enzymatic oxidation of certain serum constituents (*see* p. 101). According to B. J. Eaton,[507] rubber much lighter in color can be obtained by coagulating and drying in an atmosphere of pure carbon dioxide. T. Petch [508] has recommended warming the diluted latex to 70 or 80° C. in order to kill the enzymes. As an alternative procedure, the sheets may be warmed immediately after coagulation of the latex. C. Beadle and H. P. Stevens [509] propose to accomplish the same result by immersing the coagulum in boiling water for 10 to 15 minutes. The properties of the rubber seem to be affected adversely by this procedure, however. At the present time the above mentioned methods are scarcely used at all. The customary modern method for preventing the darkening of rubber involves the use of sodium bisulfite. Other reagents, such as formaldehyde and sodium thiosulfate, have also been recommended for the purpose. According to Edwardes,[510] crepe rubber obtained by coagulating with a mixture of sodium silicofluoride and *p*-nitrophenol is no darker than ordinary commercial "pale crepe."

The method of partial coagulation is much used for the purpose of producing especially light-colored rubber. The first step in this procedure is to add to the latex a quantity of acid insufficient for complete coagulation. The skin or lumpy mass formed by the coagulation of part of the rubber carries with it not only the impurities but also most of the yellow coloring material and the oxidizing enzymes. After separation of this mass, further addition of acid enables the production of rubber which is especially light, and sometimes even white in color.

J. Edwardes [511] recommends the addition of sodium bisulfite to the latex in the collecting vessels and agitation after the first addition of acetic acid in order to hasten agglomeration of the coagulum. After withdrawal of the first coagulum, the remaining latex is passed through a strainer (60 mesh) and is then completely coagulated by means of additional acid.

Another procedure suggested [512] for the production of light-colored rubber consists of stirring the latex continuously while gently warming, and removing the scum thereby produced.

Since extra expense is attached to the two methods mentioned above, they are used but little at the present time.

According to investigations conducted by the writer,[513] darkening in the case of *Manihot Glaziovii* may be avoided to a certain extent by treating the latex with oxalic acid, Purub, nitric acid, or hydrochloric acid as soon as possible after collection. Oxalic acid in the form of a 0.5 or 1 per cent solution gave the best results. The extent to which the properties of the rubber are injured by such a process was not investigated.

In the case of *Castilloa*, "after-darkening" may be prevented by repeated washing of the creamed rubber particles, according to C. O. Weber (*see* p. 133). This treatment removes the coloring matter and possibly the active enzymes as well. A similar method was proposed for *Kickxia elastica* by D. Spence.[514]

[507] *Dept. Agr. Federated Malay States*, Sp. Bull. No. 17, 36 (1912).
[508] Petch, T., "The Physiology and Diseases of Hevea Brasiliensis," p. 23, Dulan & Co., London, 1911.
[509] "Rubber Recueil," 358.
[510] *Bull. Rubber Growers' Assoc.*, **8**, 34 (1926).
[511] *Kautschuk*, **1**, 14 (1925) and *Bull. Rubber Growers' Assoc.*, **7**, 327 (1925).
[512] de Vries, O., "Estate Rubber," p. 392.
[513] Zimmermann, A., *Pflanzer*, **6**, 117 (1910).
[514] *Gummi-Ztg.*, **22**, 1375 (1908).

A dark coloration of the rubber can also result from the use of certain coagulating and disinfecting agents. Thus Hevea rubber, prepared by the use of phenol, pyrogallol, and picric acid, exhibits a dark color, according to G. S. Whitby.[515] Since phenol forms highly colored compounds with iron salts, care must be used to prevent contact of the damp rubber with such salts (as might occur when washing in iron vessels), in the case of Manihot rubber coagulated with phenol.

Smoking constitutes still another method by which a darkening of Hevea rubber may be produced. In most of the applications of this rubber such a coloration is not a matter of importance. In fact, the darker color is often an advantage to the manufacturer, since it covers up minor variations in color which might lead to rejection in the case of articles made from light rubber. An objection to smoked sheets, however, is that their color is not uniform. Slower drying, and the consequent greater precipitation of smoke constituents, is the explanation offered by J. C. Hartjens [516] for the presence of darker colored borders on sheets. Dark spots may result from the contact of the sheets with each other when hung up to drain, and their remaining damp longer at the points of contact.

Various Kinds of Spots

Different kinds of microörganisms can gain entrance into latex, and, if not killed in time, develop so rapidly during the coagulation and subsequent drying of the sheet or crepe rubber as to cause spots of various colors. As an example, *Bacillus prodigiosus* often produces carmine red spots in rubber. Various other bacteria, and also fungi, have been proved by T. Petch,[517] C. K. Bancroft [518] and A. Sharples [519] to be the cause of spots in rubber. According to W. Brown,[520] blue and yellow spots in crepe rubber are produced by certain species of *Fusarium* and *Penicillium*.

It is stated by N. S. Söhngen and I. G. Fol [521] that most of the living microörganisms in wet rubber do not change the physical properties of the rubber. The rubber hydrocarbon is attacked and assimilated, however, (and a lowering in viscosity thereby produced) by two species of *Actinomyces* (*A. elastica* and *A. fuscus*), which commonly occur in garden soil and in sewer water.

In combating the occurrence of these organisms, the primary consideration is that of the cleanliness of all instruments, machines, and containers with which the latex and the coagula come in contact. On plantations where infection is widely spread, a thorough cleaning of the whole establishment is recommended. A mechanical purification of the water used in washing may also be of service. Disinfecting agents should also be added to the latex, in cases of very bad infection. Quinosol (0.1 gram to each liter of latex) is especially recommended for the purpose by O. de Vries.[522] For preventing infection by fungi, H. P. Stevens [523] recommended bathing the freshly rolled sheets for three hours in a 0.1 per cent solution of para-nitrophenol or adding this reagent to the coagulant used (acetic acid or sodium silicofluoride). On another occasion, Stevens [524] proposed to accomplish the same purpose by adding dinitro-ortho-cresol to the coagulating agent.

[515] *Kolloid-Z.*, **12**, 153 (1913).
[516] *Mededeel. Proefstn. Malang.*, **27**, 13 (1919).
[517] Petch, T., "The Physiology and Diseases of Hevea brasiliensis," Dulan & Co., London, **1911**.
[518] *Dept. Agr., Federated Malay States*, Sp. Bull., **No. 16** (1913).
[519] *Ibid.*, **No. 19** (1914).
[520] *Kautschuk*, **1**, 20 (1925).
[521] *Zentr. Bakt., Parasitenk.*, Abt. 2, **40**, 84 (1914).
[522] de Vries, O., "Estate Rubber," p. 91.
[523] *Bull. Rubber Growers' Assoc.*, **7**, 560 (1925).
[524] *Bull. Rubber Growers' Assoc.*, **8**, 594 (1926).

The tendency for these discolored spots to spread can be retarded by rapid drying. Moreover, the isolation of the affected part from the sound part of the rubber, immediately after the discovery of the former, will hinder the further spread of the discoloration.

Mold

Coatings of mold often appear on dried rubber during storage and transportation. In the tropics these are generally to be attributed to the ordinary mold fungus, *Penicillium glaucum*. Since the occurrence of mold is favored by dampness, the recommended procedure is to pack the dry rubber as soon as possible, dry the cases used as thoroughly as possible in the sun, and protect the packed cases from moisture as completely as possible.

The formation of a coating of mold is also retarded by smoking, although complete protection is not afforded. In the case of sheets which are not smoked, the danger of the formation of mold is greater than with crepe rubber, since the former generally retain more moisture and serum constituents, from which the fungi can obtain nourishment. Such being the case, it is desirable to immerse the rolled-out coagula (from which sheets are to be made) in water for some time in order to dissolve out the soluble serum constituents from their surfaces. As emphasized by O. de Vries,[525] it is preferable to carry out this treatment only after the final passage of the rubber through the rolls, since otherwise it is possible again to place on the surface serum constituents which are favorable to the growth of mold.

L. R. van Dillen, C. Knaus, G. M. Kraay and R. Riebl [526] recommend immersing the coagula in a saturated solution of sodium silicofluoride for the purpose of avoiding the formation of mold. According to T. E. H. O'Brien,[527] the appearance of mold can also be prevented by placing the coagula, immediately after washing, in a 0.1 per cent solution of para-nitrophenol for one-half to one hour, or by adding to the latex one gram of para-nitrophenol for each kilogram of dried rubber. From the standpoint of the properties of the resulting rubber, this process is said not to be disadvantageous.

P. Schidrowitz and H. A. Goldsbrough,[528] O. de Vries,[529] and H. P. Stevens [530] agree in the opinion that the properties of rubber are not changed appreciably by mold, provided exposure to the mold is not prolonged. A more or less steady decrease in the weight of the rubber does occur, however. In one experiment by de Vries, for instance, the loss amounted to about 4 per cent in 40 days, 7.5 per cent in 9 months, and 31 per cent in 5 years. Since the chemical composition of the rubber sheet exposed to mold deviated but slightly from that of the fresh rubber, it seems that the mold fungus must attack the rubber hydrocarbon and the non-rubber constituents at approximately the same rate. After exposure to mold for 5 years, a distinct loss in the properties of the rubber was evident. This rubber had also become somewhat tacky.

Greasiness

"Greasiness" is the term used in the Dutch and English literature to designate a phenomenon characterized by the surfaces of sheets feeling damp to

[525] *Arch. Rubbercultuur*, **3**, 339 (1919).
[526] *Ibid.*, **12**, 61 (1928).
[527] *Rubber Res. Scheme Bull.*, 42, 1926.
[528] *India Rubber J.*, **44**, 149 (1912).
[529] *Arch. Rubbercultuur*, **11**, 279 (1927).
[530] *Bull. Rubber Growers' Assoc.*, **3**, 472 (1921); **4**, 330 (1922).

the touch, and by the formation of small drops on the surfaces when exposed to moist air. "Greasiness" results from the presence of a relatively large proportion of hygroscopic serum constituents in the sheets. It can be combated (as in the case of the formation of mold) by dissolving out the soluble material after rolling out the coagulum.

Rustiness

"Rustiness" develops principally on smoked sheets. It is characterized by the occurrence on the rubber surface of a thin dry film which tends to crack when the sheet is elongated. This film consists of serum constituents which are liberated at the surface while the sheet is still wet. The separation of the serum constituents results from the activity of aerobic microörganisms, which change these constituents into a jelly-like mass.[531]

"Rustiness" can be avoided, according to H. I. Hellendoorn, by drying the surfaces of the washed sheets as rapidly as possible, and thus giving the microörganisms no opportunity to decompose serum constituents. For this purpose, the sheets, before removal to the smoke-house, must be hung in a place exposed to draughts at sufficient distance from one another to permit of free drainage. Although soaking (extracting the rolled sheets with water) has no influence on the occurrence of "rustiness," such a procedure is advisable from the point of view of the reduction in moldiness, according to O'Brien.

The addition of quinosol to the latex or immersion of the rolled sheets in a quinosol solution is also recommended for combating "rustiness." This reagent has no deleterious effect on the properties of the rubber.[532]

The Development of Tackiness and Related Phenomena in Crude Rubber

General

From the latices of many rubber plants, notably the rubber-producing vines and various species of *Euphorbia*, there is always produced a more or less sticky or tacky rubber, regardless of the method of preparation used. It seems justifiable to attribute this tackiness to the resinous substances which invariably occur in relatively large proportions in these latices. Under certain conditions, however, it is also possible to obtain a more or less sticky mass when drying the coagulum from a latex which ordinarily yields rubber without a trace of tackiness. Moreover, crude rubber sometimes becomes tacky in storage, although it was in good condition when first produced. In extreme cases, crude rubber can harden to a varnish-like, inelastic mass, or change into an even more brittle state, from which it may finally decompose into a powder. Rubber which has reached this stage usually yields a very low grade product when vulcanized (if it can be vulcanized at all).

An absorption of oxygen and a consequent increase in weight generally accompany the changes described above. Further discussion of the chemical reactions involved is presented in the section on "Physical Testing Methods"

[531] See H. E. Hellendoorn, *Arch. Rubbercultuur*, **3**, 419 (1919); J. Groenewege, *Mededeel. Alg. Proefsta. Landbouw*, **No. 11** (1921); and T. E. H. O'Brien and M. Park, *Rubber Res. Scheme Bull.*, 31 (1923).

[532] Cf. W. Spoon, *Arch. Rubbercultuur*, **4**, 335 (1920).

of this book. Aside from oxidation, structural changes in the rubber occur. The resulting products usually behave towards solvents in a manner different from that of normal rubber. The lowered viscosity of their solutions is particularly noteworthy. These structural changes are therefore probably to be traced back to changes in the degree of polymerization.

Light and heat are two other factors which favor the development of tackiness. Certain chemical agents, especially those that are catalysts for oxidation, can also cause tackiness. Since the rubber hydrocarbon in normal crude rubber seems to be protected from oxygen by certain protective agents (proteins and resins), it is evident that tackiness is promoted by the use of agents or preparations which partially or completely destroy these protective substances. On the other hand, the development of tackiness is retarded by the addition of substances (antioxidants) which oppose the absorption of oxygen by the rubber hydrocarbon.

The observations relating to the structural changes of crude rubber only are presented in this section. The changes taking place in vulcanized rubber during aging are described in the section on "Physical Testing Methods."

The Action of Light

That dry rubber becomes tacky when it is exposed to direct sunlight has been observed by numerous authors; notably J. Parkin [533] and B. J. Eaton [534] in the case of Hevea, and A. Zimmermann [535] in the case of Manihot. Furthermore, P. Ahrens [536] was able to demonstrate that exposure to light produced tackiness. His method consisted of exposing a fine Para rubber film under a negative plate, and then dusting it with pollen, which remained attached to the tacky parts only. He was thus able to obtain a "positive" with all stages of transition.

Rubber can apparently be exposed to diffused daylight for as long as desired without becoming tacky.

Moreover, many kinds of rubber can apparently be exposed to direct sunlight without developing tackiness. K. Gorter [537] reported this to be true for a sample of Hevea rubber which was subjected to the direct light of the sun for four years.

It has been proved by different investigators that the development of tackiness is not the result of the direct action of light, but is rather to be ascribed to the fact that light promotes the oxidation of rubber. V. Henri [538] demonstrated that oxidation is essential to the development of tackiness, by exposing rubber sealed in an evacuated quartz tube, and observing the absence of tackiness.

E. Fickendey [539] also observed that rubber sealed in tubes containing only oxygen-free gases (hydrogen, nitrogen or carbon dioxide) did not become tacky, even after exposure to sunlight for weeks. On the other hand, rubber sealed in tubes with ordinary air readily became tacky, while that with pure oxygen developed a decided tackiness even more rapidly. In a further experiment by Fickendey, it was found to be possible to retain the elasticity of rubber in sunlight by keeping it under water and thus preventing the access of oxygen. Rubber exposed to the sun but stored in hydrogen peroxide be-

[533] *Roy. Botan. Gard. Ceylon, Circ.*, **1**, 151 (1899).
[534] *Dept. Agr. Federated Malay States*, Sp. Bull. No. **17**, 25 (1912).
[535] Zimmermann, A., "Der Manihot-Kautschuk," p. 250, G. Fischer, Jena, **1913.**
[536] *Chem.-Ztg.*, **34**, 266 (1910).
[537] *Dep. Landb. Nijverh. en Handel. Mededeel. over Rubber*, **1**, 4 (1911).
[538] *Caoutchouc and gutta-percha*, **7**, 4371 (1910).
[539] *Kolloid-Z.*, **9**, 81 (1911).

came tacky in a few days, whereas that similarly stored but exposed only to diffused daylight or to no light at all was kept for weeks without becoming noticeably sticky. Absorption of oxygen and increase in weight have also been observed in the case of tackiness occurring in the light.

K. Gorter [540] confirmed the observations of Fickendey by sealing samples of Borneo rubber in tubes filled with oxygen, air, hydrogen and carbon dioxide respectively, and laying them in the sun from one to eight hours each day for two weeks. At the end of this time, only the samples sealed with hydrogen and with carbon dioxide remained unchanged. The other samples had become very tacky, that sealed with pure oxygen being partially liquefied in fact.

In the case of Hevea rubber exposed to light in pure oxygen, Gorter found the absorption of oxygen to amount to 3 per cent of the weight of the rubber. When sealed with air, the oxygen absorption was but 0.6 per cent.

On the other hand, in a series of experiments involving the exposure of vine rubber and Castilloa rubber to light for months, Gorter found no appreciable increase in weight to accompany the development of tackiness. He assumed that fluctuations in the water content influenced these results.

Gorter observed a very pronounced oxidation of rubber when he brought a thin membrane (made by the evaporation of a benzene solution of rubber) into contact with oxygen in diffused daylight for a long time. At first the reaction proceeded very slowly, the absorption of oxygen being only 5 per cent of the weight of the rubber after 20 days. Upon the termination of the experiment, after 60 days, the absorption of oxygen amounted to 60 per cent.

By extraction with water, Gorter was able to isolate an aldehyde (probably levulinic aldehyde) from vine rubber which had increased in weight by 1.33 per cent while being exposed to sunlight from 1 to 8 hours a day for 6 weeks. Levulinic acid was probably also present.

Working with normal Hevea crepe, G. S. Whitby [541] observed that the quantity of material soluble in acetone changed from 2.63 to 3.23 per cent upon exposure of the crepe to direct sunlight for 3 months. The value increased to 8.33 per cent after 9 months' additional exposure. Whitby's explanation was that depolymerization, followed by oxidation, had taken place.

In contrast to these results, G. Brindejong [542] has asserted that, in the case of rubber from *Landolphia Heudelotti,* there is no increase in weight accompanying the development of tackiness in light, and that the explanation of this fact is to be traced to changes in the molecular state.

According to V. Henri,[543] ultraviolet light is especially effective in promoting tackiness. He found that crude rubber (brown Para and light plantation rubber), when exposed to the ultraviolet light from a mercury vapor lamp, developed cracks rapidly, became partially tacky, and lost its elasticity entirely. A thin sheet of rubber prepared from a benzene solution became tacky even more rapidly.

K. Asano [544] showed that it is possible for ultraviolet light to bring about changes in the structure of rubber when acting in the absence of oxygen. In his experiments, use was made of quartz test tubes transparent to light of wave lengths down to 2000 Å. The condensed spark discharge across iron and aluminum electrodes served as the source of light. The gases used were carbon dioxide, hydrogen, nitrogen and air, the latter being used for com-

[540] *Mededeel. over Rubber,* **No. 2,** 29.
[541] *Kolloid-Z.,* **12,** 191 (1913).
[542] *Z. angew. Chem.,* **21,** 1008 (1908).
[543] "Lectures on India Rubber," edited by D. Spence, p. 203, **1909.**
[544] *India Rubber J.,* **70,** 307, 347, 389 (1925).

parison. Asano found that light with a wave length below 2250 Å was especially effective in causing a rubber film, sealed in an inert gas, to become first turbid and rough, and finally wrinkled and brittle. Moreover, a large part of the rubber hydrocarbon was changed into a substance insoluble in rubber solvents. Asano considered this substance to be a polymerization product of rubber. That portion of the rubber which was still soluble showed a low viscosity in solution, and was designated as a depolymerization product of rubber. It is therefore Asano's assumption that rays of wave length around 2250 Å bring about depolymerization as well as repolymerization. In ordinary air, on the other hand, light of this same wave length caused crude rubber to become transparent and tacky. An oxidation of the rubber took place, probably preceded by depolymerization. Light having a wave length above 3100 Å had a much smaller effect, and that above 5000 Å had none whatever.

The above-described effects of light are proportional to the quantity of light absorbed. The color of the rubber also exerts an influence on the intensity of the effects.

F. Kirchhof [545] was able to show that it is possible for light to bring about the production of dark-colored substances which oppose any further oxidation, particularly in the case of sheets.

Rubber which had become tacky from exposure to the sun was shown by O. de Vries and N. Beumée-Nieuwland [546] to have an increased plasticity and a decreased viscosity. Rubber preserved in the dark did not undergo these changes.

The Influence of Temperature

That tackiness in crude rubber can often result from excessive heating during and after drying has been demonstrated by P. Schidrowitz [547] and others.

K. Gorter [548] also observed that Hevea and Ficus rubbers became tacky upon preservation for one month at 60° C., either under water or in a drying oven. He demonstrated later that an oxidation process was involved in the phenomenon. Upon heating one part of a sample for one month at 60° C. in an atmosphere of hydrogen, and the other part in air, he found that only the latter became tacky.

According to T. Marx and A. Zimmermann,[549] tackiness may be brought about by radiant heat; for example, that from a corrugated metal roof on which the sun is shining. O. de Vries [550] reports that a deleterious effect on the properties of the crude rubber does not always accompany the changes produced by heating. A normal viscosity in solution and a normal behavior upon vulcanization were exhibited by Hevea crepe which had become soft and tacky as a consequence of heating. De Vries designates this phenomenon as "stickiness," to distinguish it from "tackiness," which latter phenomenon is accompanied by a decided change in physical properties.

According to H. Pohle,[551] the change of normal rubber into tacky rubber (which he designated as modification γ) can be accomplished by oxygen, by sunlight, or by steady heating. He emphasized, however, that no absorption of oxygen takes place, and that the oxygen merely brings about depolymerization.

[545] *Kautschuk*, **3**, 243 (1927).
[546] *Arch. Rubbercultuur*, **11**, 563 (1927).
[547] Schidrowitz, P., "Rubber," 2nd ed., p. 136, Methuen & Co., Ltd., London, **1916**.
[548] *Dep. Landb. Nijverh. en Handel. Mededeel. over Rubber*, **1**, 4 (1911); **2**, 24 (1912).
[549] *Tropenpflanzer*, **25**, 39 (1922).
[550] de Vries, O., "Estate Rubber," p. 362.
[551] *Kolloidchem. Beihefte*, **13**, 32 (1921).

Mechanical Working

K. Gorter [552] found that the surface of Hevea crepe became somewhat tacky upon passing it 100 times through a mill with smooth rolls. Possibly the effect of heat can account for the tackiness produced. According to T. Marx and A. Zimmermann,[553] neither damp nor dry rubber is rendered tacky by mechanical working, provided no appreciable development of heat accompanies the working.

Bacteria

Since rubber to which antiseptic agents (especially creosote) had been added did not become tacky upon exposure to sunlight, K. Bamber [554] concluded that the development of tackiness is to be traced back to the action of bacteria. On the other hand, P. Schidrowitz [555] found that antiseptic agents did not retard the development of tackiness in the least. Moreover, it was reported by G. Bertrand [556] that African rubber obtained directly by boiling the latex was more subject to tackiness than that resulting from coagulation in the cold. He also stated that the development of tackiness was most rapid in direct sunlight, despite the fact that the sun's rays are destructive to microörganisms.

T. Marx and A. Zimmermann [557] were not able to establish any relationship between putrefaction and tackiness, in the case of Manihot rubber.

It seems probable, therefore, that bacteria do not cause tackiness in rubber as a general rule. It was demonstrated by D. Spence,[558] however, that they may favor tackiness indirectly by converting the proteins of the rubber into acidic substances which constitute a suitable medium for the development of tackiness. The same view was expressed by G. Bertrand.[559] K. Gorter [560] also observed that when sheets were placed one upon another, putrefaction occurred and moisture was liberated at certain places. It was at these places that tackiness started and from them spread to other parts of the sheets. V. Henri,[561] working with rubber of different origin, also observed that a brown coloration, softness, and tackiness were to be found at places on which fungi had developed.

Method of Coagulation

According to F. Frank,[562] tacky rubber is obtained when the rubber of the latex, which is in a low state of polymerization, is not converted immediately upon coagulation into rubber of a high degree of polymerization. Such a situation may occur, for example, in the case of coagulation in large lumps. Portions of the latex which have not been coagulated at all, or have at best been changed only into rubber of a low state of polymerization, are frequently inclosed in such lumps. From observations made on Kickxia and Manihot, F. Frank and E. Marckwald [563] concluded that the more rapid the coagulation, the higher is the state of aggregation.

The statement of F. Ripeau [564] that rubber obtained from diluted latex becomes tacky in the sun, whereas that from concentrated latex does not, was

[552] *Dep. Landb. Nijverh. en Handel. Mededeel. over Rubber*, **No. 2** (1912).
[553] *Tropenpflanzer*, **25**, 40 (1922).
[554] "Lectures on India Rubber," edited by D. Spence, p. 201, **1909.**
[555] Schidrowitz, P., "Rubber," 2nd ed., p. 136, London, **1916.**
[556] *Gummi-Ztg.*, **20**, 1018 (1906).
[557] *Tropenpflanzer*, **25**, 85 (1922).
[558] *Kolloid-Z.*, **4**, 70 (1909).
[559] "Lectures on India Rubber," edited by D. Spence, p. 200, **1909.**
[560] *Dep. Landb. Nijverh. en Handel. Mededeel. over Rubber*, **1**, 3 (1911).
[561] *Caoutchouc and gutta-percha*, **7**, 4371 (1910).
[562] *Pflanzer*, **5**, 177 (1909), and *India Rubber J.*, **61**, 1237 (1911).
[563] *Pflanzer*, **6**, 257 (1910); *Gummi-Ztg.*, **25**, 877 (1911); and *Kolloid-Z.*, **5**, 189 (1909).
[564] Ripeau, F., "Caoutchoucs amazoniens et asiatiques," p. 39, Paris, **1914.**

not confirmed by Riebl, according to O. de Vries and N. Beumée-Nieuwland.[565] On the other hand, latex very much diluted (to 50 times its original volume) gave tacky rubber when coagulated with acetic acid, but not when coagulated with aluminum chloride.[566]

The literature contains very divergent opinions regarding the influence of the protein content upon the tackiness of rubber. According to F. Frank,[567] rubber rich in proteins is especially susceptible to the development of tackiness. On the other hand, Spence's [568] observations indicated that the probability of tackiness is greatest with rubbers containing the very smallest proportions of proteins. The same opinion is also held by J. Groenewege,[569] but not by O. de Vries and N. Beumée-Nieuwland.[570] The latter investigators observed that rubber prepared with papain did not become tacky.

It has been stated by P. Schidrowitz [571] that alkalies favor the occurrence of tackiness. B. J. Eaton [572] has also observed that the rubber obtained after immersing the coagulum in an alkaline solution easily becomes tacky.

Rubber prepared from ammonia-preserved latex does not, in general, tend toward tackiness, according to O. de Vries and N. Beumée-Nieuwland.[573] Only the top layer of the cream which forms on such latex yields rubber which readily becomes tacky.

De Vries and Beumée-Nieuwland [574] report that a product which very easily becomes tacky is obtained from the pasty mass resulting from the addition of a strong solution of caustic soda to Hevea latex. The caustic solution apparently forms a substance which causes tackiness (especially in an alkaline medium) but which can be almost completely removed by washing. Furthermore, these investigators [575] state that, when the tackiness is produced by alkalies, the rubber becomes soft, sticky and opaque, and finally so loses its shape that a doughy mass results. This mass may remain soft and sticky for a year or so, and becomes hard only after a very long time, if at all. Light plays no part in causing tackiness of this type.

It is stated by de Vries and Beumée-Nieuwland [576] that rubber obtained from strongly acidified latex by partial neutralization, or by allowing separation to take place gradually and spontaneously, shows a pronounced tendency to develop tackiness, especially in the light. An increase in weight, amounting to from 4 to 12.5 per cent, may accompany this phenomenon.

O. de Vries and H. I. Hellendoorn [577] observed that crepe prepared by the use of hydrochloric acid had become entirely tacky after 2 years. In the case of rubber of this type, tackiness is strongly favored by light, according to de Vries and Beumée-Nieuwland. In the dark, such rubber may remain in good condition. A 9 to 12 per cent increase in weight accompanies the development of tackiness. Such rubber is rather rapidly transformed into a bright yellow mass, which remains transparent, and which soon becomes hard as glass.

D. Spence [578] found that Kickxia latex, when treated with a solution (0.1 per cent) of sulfuric acid at 35° C. for about one month, yielded rubber

[565] *Arch. Rubbercultuur*, **11**, 567 (1927).
[566] See de Vries and Beumée-Nieuwland, *ibid.*, **11**, 567 (1927).
[567] "Lectures on India Rubber," edited by D. Spence, p. 201, **1909.**
[568] *Ibid.* (Discussion).
[569] *Arch. Rubbercultuur*, **8**, 644 (1924). *Ibid.*, **11**, 569 (1927).
[571] Schidrowitz, P., "Rubber," 2nd ed., p. **137**, Methuen & Co., Ltd., **1916.**
[572] *Agr. Bull. Federated Malay States*, **4**, 30 (1915) and Sp. Bull. **No. 27**, 307 (1918).
[573] *Arch. Rubbercultuur*, **11**, 567 (1927).
[574] *Ibid.*, **9**, 760 (1925).
[575] *Ibid.*, **11**, 567 (1927).
[576] *Ibid.*, **11**, 567 (1927).
[577] *Ibid.*, **4**, 209 (1920).
[578] *Kolloid-Z.*, **4**, 71 (1909).

which was completely tacky. In the control experiment without sulfuric acid, rubber of normal nerve was obtained. An appreciable increase in weight had not accompanied the development of tackiness. Moreover, the acetone extract of the tacky sample was only slightly greater than that of the control sample. The viscosity of the chloroform solution of the normal rubber was 50 per cent greater than that of the tacky rubber. Spence attributed the tackiness to chemical changes or to changes in the state of aggregation of the rubber. In contrast to the results of Spence, F. Frank and E. Marckwald [579] reported that rubber obtained from Kickxia latex by using sulfuric acid was not especially susceptible to tackiness. Working with Hevea latex, de Vries [580] obtained results similar to those of Frank and Marckwald.

Manihot rubber which had been coagulated by means of a mixture of the juice and fibers of certain species of *Cissus* with a solution of calcium chloride, readily became tacky when exposed to light and heat, according to T. Marx and A. Zimmermann.[581]

Tackiness was not promoted by the use of the sap of the plant alone as the coagulant. Furthermore, coagulation with calcium hydroxide yielded rubber which became tacky more slowly than did the others tested.

Substances Promoting the Development of Tackiness

That copper salts contribute to the development of tackiness has been observed by numerous investigators. B. J. Eaton [582] was probably the first to observe this fact in the case of Hevea rubber. Within a short time after adding copper sulfate to rubber, or immersing the rubber in a solution of this salt, tackiness was to be observed. Similar observations were made by E. Fickendey [583] and by A. Zimmermann [584] in the case of Manihot rubber. Tackiness induced by cupric sulfate develops in the dark as well as in the light.

In plantation practice, copper may find its way into the rubber through the use of acetic acid contaminated with traces of copper, or from the parts of the washing mills and other machinery containing copper. Copper in the lubricating oils used is also a source of trouble. According to A. Sharples,[585] the introduction into the latex of copper in amounts sufficient to cause tackiness is not to be feared from treating the trees with Bordeaux mixture, provided sufficient care is used in the treatment.

A considerable increase in the portion of the rubber soluble in acetone takes place when tackiness is produced by copper salts. Acetone dissolved 71.3 and 78.0 per cent of some very tacky samples examined by G. S. Whitby.[586] Moreover, O. de Vries [587] has observed solubilities in acetone as high as 93 per cent. The increases in weight of samples developing tackiness (induced by copper) were from 7 to 13.5 per cent in fourteen weeks, according to S. Morgan.[588]

B. J. Eaton,[589] E. Fickendey,[590] A. Zimmermann,[591] and T. Marx and A. Zimmermann [592] concur in the opinion that iron salts likewise favor the development of tackiness.

[579] *Kolloid-Z.*, **5**, 189 (1909).
[580] de Vries, O., "Estate Rubber," p. 178.
[581] *Tropenpflanzer*, **25**, 36 (1922).
[582] *Dept. Agr. Federated Malay States*, Sp. Bull., **No. 17**, 26 (1912).
[583] *Kolloid-Z.*, **9**, 81 (1911).
[584] Zimmermann, A., "Der Manihot-Kautschuk," p. 257, G. Fischer, Jena, **1913**.
[585] *India Rubber J.*, **54**, 193 (1917).
[586] *India Rubber J.*, **45**, 1043 (1913).
[587] de Vries, O., "Estate Rubber," p. 618.
[588] Morgan, S., "Preparation of Plantation Rubber," p. 164, London, **1913**.
[589] *Dept. Agr. Federated Malay States*, Sp. Bull., **No. 17**, 23 (1912).
[590] *Kolloid-Z.*, **9**, 81 (1911).
[591] Zimmermann, A., "Der Manihot-Kautschuk," p. 257, G. Fischer, Jena, **1913**.
[592] *Tropenpflanzer*, **25**, 84 (1922).

Washing the coagula with solutions of manganese salts or of potassium permanganate does not promote tackiness, according to de Vries.[593] K. Gorter [594] also found no difference in the manganese contents of the tacky and of the sound parts of a given sample of rubber.* From Manihot latex which had been treated with potassium permanganate, A. Zimmermann [595] obtained a sheet which did not become tacky in the dark nor in diffused light, but which was covered with a brittle, varnish-like layer. The rubber beneath this layer was almost entirely devoid of nerve.

From samples of Manihot latex coagulated with potassium dichromate and potassium chromate, A. Zimmermann [596] obtained rubber which showed no trace of tackiness and no loss in extensibility and nerve after seven months.

K. Gorter [597] quotes Thompson to the effect that rubber on which oil has been rubbed forms a soft mass, which retains its elasticity at first, but which oxidizes rapidly in the air. Palm oil was observed to have the greatest effect among the oils tested, whereas castor oil had the least.

Oxidizing Enzymes

It was assumed by K. Bamber [598] that an oxidase plays a part in the development of tackiness in rubber. He observed that heating the coagulum at 100° C. retarded the development of tackiness, and assumed that the death of the oxidase accounted for the retardation. On the other hand, D. Spence [599] repeatedly observed the development of very pronounced tackiness on samples of rubber in the preparation of which great care had been used to remove the enzymes before coagulation. Furthermore, the oxidase present is not made inactive by boiling the rubber, according to Spence. Certain observations made by K. Gorter [600] during experiments on solutions of rubber in benzene led that investigator to oppose the idea that oxidizing enzymes bring about tackiness. A. van Rossem [601] was not able to confirm these observations. T. Petch [602] was also unable to detect any spreading of the tackiness, when normal rubber was brought into intimate contact with tacky rubber. Similar observations were made by A. Zimmermann [603] and by T. Marx and A. Zimmermann,[604] in the case of Manihot rubber.

The Prevention of Tackiness

Oxidation, and also tackiness, can be prevented by the addition of tannin to the latex, according to E. Fickendey.[605] He observed that rubbers prepared from Hevea, Kickxia and Ficus latices by using 2 to 5 per cent of tannin, were still unharmed after several days in the sun, while those coagulated without tannin had long since become tacky. The degree of protection increased with the quantity of tannin employed.

[593] de Vries, O., "Estate Rubber," p. 366.
[594] *Mededeel. over Rubber*, **2**, 48 (1912).
* Translator's Note. The work of other investigators indicates that manganese in certain forms may have a very deleterious effect on rubber. Thus Bruni and Pelizzola [*India Rubber J.*, **62**, 101 (1921)] caused the rapid development of tackiness by incorporating manganese dioxide in crude rubber. Moreover, upon analyzing various samples of tacky rubber, they found a distinct correlation between the manganese content and the degree of tackiness. (*Also see* page 613 in this book.) V.N.M.
[595] Zimmermann, A., "Der Manihot-Kautschuk," p. 257, G. Fischer, Jena, **1913.**
[596] Zimmermann, A., "Der Manihot-Kautschuk," p. 257, G. Fischer, Jena, **1913.**
[597] *Mededeel. over Rubber*, **1**, 49 (1911).
[598] "Lectures on India Rubber," edited by D. Spence, p. 201, **1909.**
[599] *Kolloid-Z.*, **4**, 71 (1909), and *Gummi-Ztg.*, **22**, 1375 (1908).
[600] *Mededeel. over Rubber*, **2**, 40 (1912).
[601] *Kolloid-Z.*, **12**, 78 (1913).
[602] Petch, T., "The Physiology and Diseases of Hevea Brasiliensis," p. 253, Dulan & Co., Ltd., London, **1911.**
[603] Zimmermann, A., "Manihot-Kautschuk," p. 256, G. Fischer, Jena, **1913.**
[604] *Tropenpflanzer*, **25**, 86 (1922).
[605] *Kolloid-Z.*, **9**, 81 (1911).

R. Ditmar [606] states that the development of tackiness can be prevented by treating the rubber with formaldehyde or with a mixture of formaldehyde and benzene, or by dusting it with colloidal clay.

Damp rubber seems to be less subject to tackiness than dry rubber, probably as a consequence of the fact that oxygen is capable of penetrating dry rubber more readily than rubber still saturated with water. In order to prevent the injurious effects of pressure and heat during storage and transportation, it is recommended by F. Frank [607] that some water be left with the rubber when it is packed. According to T. Marx and A. Zimmermann,[608] damp, freshly coagulated rubber can remain exposed to direct sunlight for several hours without exhibiting any evidence of tackiness when dried.

Influence of Method of Preparation on Chemical Composition

The statement that crude rubbers obtained from quite similar latices may vary considerably in chemical composition, according to the method of preparation used, scarcely requires elaboration. As an instance, the fact may be mentioned that rubber prepared by drying whole latex retains all of the serum constituents, whereas that from centrifuged latex contains rubber particles almost exclusively. Moreover, the chemical changes taking place during preparation—especially the maturation which may occur in rubber which is still damp—are capable of exerting an influence on the chemical composition of the crude rubber.

Water Content and Hygroscopicity

The variations in the water content of different kinds of crude rubber can be traced primarily to the methods of preparation, since some methods allow a more complete removal of water than others. In the case of Para (wild) rubber, for instance, the smoking process used does not permit of the complete removal of moisture from the individual layers of rubber. When the completed ball is formed, moisture can escape only from the outer layers. As a consequence, the inner part of the ball retains so much water that the loss on washing (largely due to the moisture present) is generally 10 to 20 per cent, while the similar loss in the case of crepe rubber seldom exceeds 1 per cent. The water contents of other "whole," air-dried rubbers are also relatively large, as a consequence of the hygroscopic substances present. As an example of this fact, A. van Rossem [609] has reported that samples of rubber obtained by evaporating Hevea latex contained approximately 4 per cent, smoked sheets an average of 0.61 per cent, and crepe rubber 0.42 per cent of water. It has also been proved [610] that the degree of dilution, the duration of soaking of the coagula, and the addition of hygroscopic salts can exert an influence on the content of hygroscopic material and consequently on the water content of air-dried crepe and sheet rubber.

Resin Content

P. Schidrowitz and F. Kaye [611] have reported that the resin contents of samples of crude rubber made from the same latex may vary with the method

[606] *Gummi-Ztg.*, **41**, 1688 (1927).
[607] *Pflanzer*, **5**, 177 (1909).
[608] *Tropenpflanzer*, **25**, 37 (1922).
[609] *Kolloidchem. Beihefte*, **10**, 41 (1919).
[610] de Vries, O., "Estate Rubber," p. 607.
[611] *India Rubber J.*, **34**, 377 (1907), and *J. Soc. Chem. Ind.*, **26**, 1264 (1907).

of coagulation used. In the case of *Kickxia elastica,* they found this variation in resin content was from 5.30 to 7.82 per cent, calculated on the basis of the dry rubber. (By working the samples with a solvent for resins, it was found possible to reduce the resin content to 1.74 per cent.) An unusually high proportion of resin (8.76 per cent) resulted when the coagulation was carried out with formaldehyde. The experiments of F. Eduardoff [612] indicated the ratios of pure rubber to resin obtained upon the coagulation of the latex of *Kickxia elastica* with various agents to be as follows:

2% Crude creosote	100:10
98% Alcohol	100:12
2% Coalatex	100:19
2% Carbolic acid	100:21

At the present time it seems improbable that any method of preparation can be developed which will permit of the production of resin-free rubber without the use of solvents for resins. The above described variation of the resin content with the method of preparation may result from the variation in the quantities of acetone-soluble products formed by chemical reaction during preparation.

Compounds Containing Nitrogen

Since the nitrogenous compounds in latex are partly soluble in water, and since they behave differently towards the various coagulants, it is apparent that the method of coagulation should have an influence on the quantities of such compounds in crude rubber. According to A. van Rossem,[613] the determinations of the quantities of nitrogen present indicate the protein contents of various rubbers to be as follows: Hevea sheet and crepe rubber—an average of 2.82 per cent; Para rubber—somewhat less than 2 per cent; and Kerbosch rubber (obtained by drying latex)—4.7 to 5.3 per cent. O. de Vries [614] states that about one-third of the substances containing nitrogen remain in the serum, in the case of the normal coagulation of Hevea latex with acetic acid. Although some of these nitrogenous compounds are precipitated by boiling the serum, most of them remain in solution.

With many methods of preparation, particularly those in which the rubber is not freed from water for a long time, it is possible for extensive decompositions of the nitrogenous compounds to take place.

Other Serum Constituents

The proportion of the water-soluble serum constituents which is held by the coagulated rubber varies with the method of preparation used. According to O. de Vries,[615] this proportion is lowest in the case of good washed crepe, from which only 0.2 to 0.45 per cent of the weight of the rubber can be extracted with water. From smoked sheets, on the other hand, 0.6 to 2.0 per cent is extractable. Only about 5 per cent of water-soluble substances can be removed from evaporated latex, despite the fact that the original latex contained soluble substances corresponding to 10 to 12 per cent of the rubber present. It appears that over half of these substances must either become insoluble upon drying or become adsorbed by the rubber particles.

[612] *Gummi-Ztg.,* **22,** 387 (1908).

[613] *Kolloidchem. Beihefte,* **10,** 61 (1919).

[614] de Vries, O., "Estate Rubber," p. 20 and 253.

[615] de Vries, O., "Estate Rubber," p. 612.

It is a noteworthy fact that Para rubber generally contains no greater amount of serum constituents than normal crepe and sheet rubber. This circumstance is undoubtedly to be explained on the basis of the separation ("sweating out"; *see* p. 108) of a large part of the serum during the drying of the large Para balls.

The following average values for the ash content of various rubbers were obtained by A. van Rossem:[616] crepe 0.30 per cent; sheets 0.38 per cent; and Kerbosch rubber 1.0 to 1.8 per cent.

Acid Content

The acid content of various kinds of rubber has also been the subject of considerable investigation. The results obtained by Beadle and Stevens[617] (with acidity expressed as percentage of acetic acid) are as follows:

	Per Cent
Sheets	0.150 - 0.292
Crepe	0.017 - 0.120
Para rubber	0.120 - 0.168

Considerably larger quantities of acid—up to 0.4 per cent—have been found in wild (Para) rubber by other investigators.[618] The frequently claimed superiority of this latter rubber over plantation rubber obviously cannot be based on its smaller acid content.

According to W. Crossley,[619] the quantity of acid retained by coagulated rubber is dependent primarily upon the concentration of the acidic coagulating agent, but also upon the nature of the acid used. A part of the acid can be easily washed out with water, while the remainder is bound by adsorption.

[616] *Kolloidchem. Beihefte*, **10**, 57 (1919).

[617] *India Rubber J.*, **41**, 15 (1911).

[618] See O. de Vries, "Estate Rubber," p. 613

[619] *India Rubber J.*, **18**, 11 (1911), and *Kolloid-Z.*, **12**, 49 (1913).

The Chemistry of Rubber *

By R. Pummerer and A. Koch†

General

The Rubber Hydrocarbon and Accompanying Substances in Latex

As previously stated (p. 59) rubber latex is a dispersion. A partially colloidal solution of sugars, resins and proteins constitutes the continuous phase while the microscopic and ultramicroscopic rubber particles form the dispersed phase.

Although the rubber hydrocarbon is present in latex as a compound of high molecular weight, the work of C. O. Weber [1] seemed to indicate the opposite. Weber investigated the latex of Brazilian *Castilloa elastica* as it came from the tree and concluded from his results that the rubber hydrocarbon was present in the latex as a compound of low molecular weight. By extracting the fresh latex with ether, he succeeded in isolating the rubber hydrocarbon as a colorless oil. Only after the addition of a trace of formic acid, accompanied by a rise in temperature to 61° C., was the oil supposed to have been polymerized to the true rubber molecule. Weber assumed the oil to be a diterpene of the formula $C_{20}H_{32}$.

The opinion generally accepted today was first advanced by Harries,[2] after his investigation in Sicily, of two latices, *Ficus magnolii Borci* and *Ficus elastica*. He extracted the rubber from the fresh latex with ether, and obtained from the ether extract a crystalline substance for which the analysis corresponded to the formula $C_{30}H_{48}O_3$. The freshly extracted rubber differed only in solubility from extracted rubber which had been allowed to stand. It gave a normal nitrosite C and otherwise exhibited all the properties of rubber. There was no similarity to an aliphatic diterpene. Moreover, after standing a short time, its solubility became that of normal rubber. Harries attributed the greater solubility of the freshly extracted material to differences in degrees of aggregation of the two rubbers. Eduardoff [3] reached similar conclusions from his own work with fresh latex.

Hinrichsen and Kindscher [4] studied the molecular size of the rubber hydrocarbon in latex by conducting molecular weight determinations directly on the benzene extract of latex. After correcting for the non-rubber constituents in solution with the rubber, these investigators arrived at the value 3,170 as the lower limit of the molecular weight of rubber. An exact determination by this method would hardly be possible. Even on the basis of these uncertain determinations, however, the presence of an aliphatic diterpene is precluded. Viscosity measurements by van Rossem [5] on rubber solutions obtained by extracting latex with benzene also point to a high molecular weight.

† Translated by R. F. Dunbrook.

* The chart on page 161 gives a summary of the reactions of the rubber hydrocarbon which are discussed in this section of the book.

[1] *Ber.*, **36**, 3108 (1903).
[2] *Ber.*, **37**, 3842 (1904).
[3] *Gummi-Ztg.*, **23**, 809 (1909).
[4] *Ber.*, **42**, 4329 (1909).
[5] *Kolloidchem. Beihefte*, **10**, 9 (1918).

The rubber hydrocarbon of high molecular weight is therefore synthesized the plant. No one has ever again succeeded in isolating from latex an oil [Weber] which is polymerized by traces of acid. A molecular weight , which is the only reliable evidence that would substantiate Weber's observation, is lacking. The oily nature of the product is no proof of the presence of a hydrocarbon of low molecular weight. Impure rubber obtained from its solutions is frequently oily, and usually contains from one to three per cent of oxygen. The temperature (61° C.) recorded by Weber is of considerable significance.

Sugars, resins, proteins, and other organic substances always accompany rubber in latex. The literature is very extensive on this subject, as these substances are of great importance in connection with the evaluation and the processing of rubber.

Sugars. Starch, which frequently occurs in other latices, is not found in the most important ones, although it is present in large quantities in the cells adjacent to the laticiferous elements. Among other types of sugars, L. R. Dillen[6] believes that galactose, glucose, and possibly fructose are present. They do not occur uncombined and are present only in small quantities (0.3 to 0.4 per cent). Cane sugar is not found in Hevea latex. A thorough investigation of the sugars in latex would be of real value, since the synthesis of the hydrocarbon by the plant probably proceeds in some manner through the assimilation of the carbohydrates. Further encouragement for this idea is given by the very creditable hypothesis of O. Aschan,[7] who holds that isoprene is formed in the plant from acetone and acetaldehyde. It is known that these two substances can actually be prepared from hexoses by fermentation.

Girard[8] isolated from latex a well-crystallized, optically inactive, sugar-like substance (melting point 195° C.), having the empirical formula, $C_6H_{10}O_5$. In a careful investigation by Maquenne,[9] the product was later identified as dimethyl-*i*-inositol, $C_6H_6(OH)_4(OCH_3)_2$. This investigator[10] also found monomethyl-*d*-inositol in latex, and de Jong[11] established the presence of monomethyl-*l*-inositol, a substance also contained in Quebracho bark. According to Gorter[12] it constitutes 1.45 per cent of the latex, and the proportion, according to Spoon,[13] is quite constant.

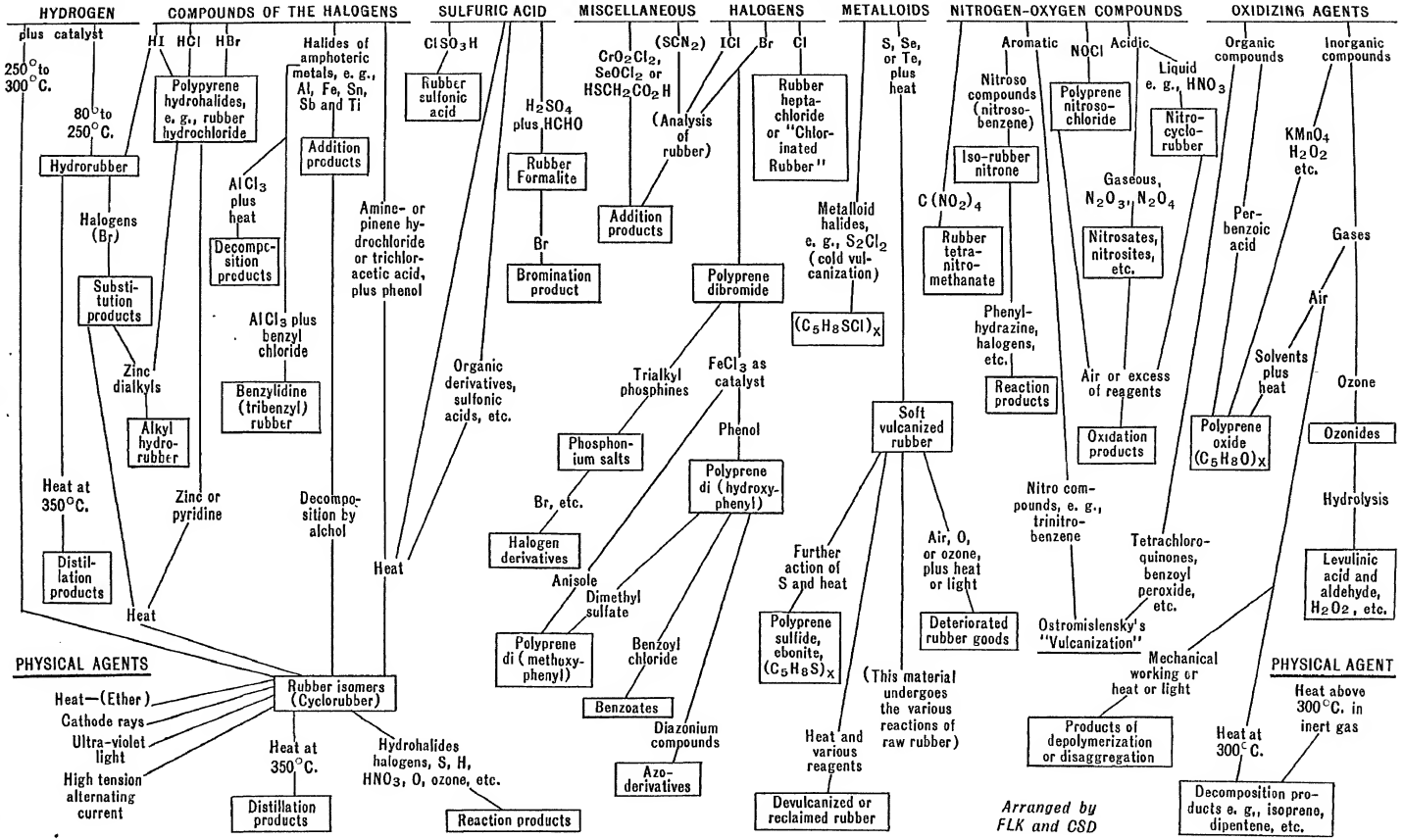
Resins. These substances constitute the acetone-soluble portion of latex. After coagulation, they are present in both the rubber and the serum.* This class includes a series of alcohols related to phytosterin, most of which have been isolated from the acetone extracts of various kinds of crude rubber. Attention is directed to the systematic compilation of Hillen,[14] covering the rubber resins. The resin content varies in high grade rubbers from 1 to 3

[6] *Arch. Rubbercultuur*, **6**, 623 (1922); also R. H. Dillen, *Arch. Sprutje*, **11**, 334 (1897).
[7] *Ann.*, **461**, 13 (1928).
[8] *Compt. rend.*, **67**, 822 (1868); **73**, 426 (1871); **77**, 995 (1873).
[9] *Compt. rend.*, **104**, 1853 (1887).
[10] *Ann. chim. phys.* (6), **12**, 566 (1887), also Flint and Tollens, *Ann.*, **272**, 288 (1893).
[11] *Rec. trav. chim.*, **25**, 48 (1906).
[12] *Arch. Rubbercultuur*, **1**, 376 (1917).
[13] *Ibid.*, **5**, 53 (1921). According to this author and de Vries, *ibid.*, **7**, 399 (1923), the sugar content is higher in the latex of infrequently tapped trees than in that of trees tapped more often.

* Translator's Note. By the cold extraction with ether of the serum remaining after coagulation of Hevea latex with alcohol, E. Rhodes and R. O. Bishop [*Quart. J. Rubber Research Inst. Malaya*, **2**, 124 (1930)] have obtained a material which is a peculiar complex of fatty acids, sugar, ether soluble phosphorus compounds, and nitrogen. This material possesses properties abnormal to fatty bodies other than the ill-defined class called lipins. This lipin from latex has been found by B. J. Eaton, E. Rhodes and R. O. Bishop [*Ibid.*, **2**, 136 (1930)] to exert considerable accelerating effect on fast-curing rubbers, such as slab rubber, but only slight accelerating effect on smoked sheets or pale crepe.

[14] Hillen, "Kautschuk- und Guttaperchaharze." Dissertation, Bern (1913). See also Gottlob, "Technologie der Kautschukwaren," p. 79, Vieweg, Braunschweig, **1925.**

REACTIONS OF THE RUBBER HYDROCARBON
RUBBER, $(C_5H_8)_x$ (POLYPYRENE)



Arranged by FLK and CSD

per cent, while inferior grades of eastern Asiatic varieties, such as jelutong, may contain 40 per cent or more of resins. Resins of the nature of optically active phytosterin are unsaponifiable. Saponifiable resins are also present in latex, as well as those arising from the oxidation of the rubber hydrocarbon. Oxidized rubber contains much resinous material.

Proteins.[15] Proteins are present in latex to the extent of 1.5 to 2 per cent, and form part of the insoluble residue when rubber is dissolved. Little is known concerning their chemical constitution.[16]

Bruni and Levi[17] obtained *alpha*-aminovaleric and *alpha*-aminocaproic acids in 10 per cent yields from the acetone extract of vulcanized slabs.

Organic acids that have been identified are as follows: hydrocyanic,[18] malonic, palmitic, stearic,[19] and small quantities of levulinic acid, the last being a well-known oxidation product of rubber.

Latex as it flows from the *Hevea* tree, usually reacts slightly acid (pH 6.0) or, very seldom, neutral.* With the addition of acid, coagulation begins at pH 4.8 and is complete at pH 4.5. If acid is added rapidly to pH 3, coagulation is avoided. Further addition of acid causes coagulation.[20] Molisch[21] tested with litmus the milky saps of forty-two different varieties of plants, among which, however, there was none distinctly of the rubber type. He found an acid reaction in most cases, neutral reaction rarely, and never an alkaline one. Moulay[22] reports an acid reaction for *Manihot Glaziovii,* as does also Adriani[23] and Burgess[24] for *Ficus clastica,* Lock[25] for *Castilloa clastica,* and Spence[26] for *Kickxia clastica.*

The literature records widely deviating results for the measurement of the acid reaction of Hevea latex. This is probably due to the fact that different authors used different indicators. According to O. de Vries,[27] fresh Hevea latex always reacts acid to phenolphthalein, is usually alkaline toward litmus, though at times very near the color change, and is always alkaline to methyl red or methyl orange. Freundlich and Hauser[28] state that the pH value of fresh latex averages 6.0 and gradually rises to 6.25 as carbon dioxide is evolved. Bobilioff[29] has found that the cells surrounding the latex vessels always show a strongly acid reaction. The acidity in these cells increases with frequent tapping as it does in latex.

Other organic foreign substances which have been observed include acetaldehyde[30] and methylamine. The former can be detected by its odor, and is especially deserving of mention, since it has been suggested that isoprene may be formed from acetaldehyde and acetone.

[15] Beadle and Stevens, *Kolloid-Z.*, **11,** 61 (1912); Schmitz, *Chem.-Ztg.*, **27,** 1085, 1131 (1903); *Ber.*, **28,** 1743 (1914); Spence, *India Rubber J.*, **54,** 766 (1917); **35,** 23 (1907).

[16] If the nitrogen content is multiplied by the "protein factor" (6.25) the approximate protein content is obtained. There are also protein glucosides present. See Spence and Kratz, *Kolloid-Z.*, **15,** 217 (1914).

[17] *Chem. Zentr.*, **98,** II, 513 (1927); *Giorn. chim. ind. applicata*, **9,** 161 (1927).

[18] According to Bobilioff, *Arch. Rubbercultuur*, **11,** 177 (1927), chiefly in the laticiferous elements of young plants.

[19] A. J. Ultée, *J. Soc. Chem. Ind.*, **41,** 948A (1922).

* Translator's Note. According to recent work by Hauser and Scholz, the pH of freshly tapped latex lies between 7.2 to 7.0. This figure remains constant over a period of several hours and then suddenly drops to pH 6.9 to 6.7 and the latex coagulates. See "Latex," by E. A. Hauser, translated by W. J. Kelly, p. 88, Chemical Catalog Co., Inc., New York, **1930.**

[20] O. de Vries and N. Beumée-Nieuwland, *Arch. Rubbercultuur,* **10,** 548 (1926).

[21] Molisch, H., "Studien über den Milchsaft und Schleimsaft der Pflanzen," p. 43, G. Fischer, Jena, **1901.**

[22] *L'agric. prat.*, **5,** 369 (1905).

[23] *Jahresber. Fortschr. Chem.*, 520 (1851).

[24] *Agr. Bull. Str. Federated Malay States,* 18 (1905).

[25] "Rubber and Rubber Planting," p. 28, Cambridge, **1913.**

[26] *Chem. Zentr.*, **79,** I, 742 (1908).

[27] *Arch. Rubbercultuur,* **7,** 173 (1923).

[28] *Kolloid-Z.,* supplementary volume, **36,** 18 (1925).

[29] *Arch. Rubbercultuur,* **9,** 474 (1925).

[30] M. Kerbosch, *Rec. trav. chim.*, **34,** 235 (1915); *Rubber Recueil,* p. 361, 1914; see also de Vries, "Estate Rubber," p. 25.

Coloring Matter. Most latices are white as they flow from the plant. It was early noticed [31] that certain *Hevea* trees produce latex with a more or less intense yellow color which, according to de Vries,[32] disappears after continuous tapping. By means of fractional coagulation the coloring matter, which is as yet unidentified, can be concentrated in one fraction, leaving the remainder pure white. Smoking produces a reddish-brown color (as in smoked sheets), which is possessed by all fractions, and which therefore has no connection with the above-mentioned yellow color. On extracting the smoked sheets with acetone* or ether, the color is quickly removed, with the formation of an orange-yellow extract.[33]

Enzymes. Peroxydases as well as oxydases which are especially active in slightly acid solutions have been found in latices. Spence [34] reported a peroxydase in Hevea latex which became inactive on warming to 100° C. The darkening that occurs in cut Para rubber when exposed to the air could not be prevented, however, by heating for one hour at 100° C. Whitby [35] could find no oxydase, but was able to demonstrate the presence of a peroxydase which withstood temperatures of 70° C., but not 90° C. Furthermore, he assumes the presence in latex of a protein-splitting ferment (protease) which may perhaps play a role in coagulation when it occurs spontaneously and is not brought about by means of acetic acid or formic acid.

Inorganic Constituents. Potassium, magnesium, calcium, phosphoric acid,[36] and sulfuric acid were determined in latex by Beadle and Stevens. These authors give in Table 1 [37] the analytical results for the latex constituents of three samples.

TABLE 1.—*Composition of Latex.*

		Per cent by weight of the latex		
		A	B	C
Total solid constituents in original latex		30.0	22.0	25.8
Total solid constituents in the dialyzed portion		2.61	1.65	1.52
In the dialysate	Sugar after inversion	0.24	0.19	0.15
	Nitrogen (diffusible)	0.048	0.054	0.043
	Nitrogen, as protein	0.30	0.34	0.27
	Sulfuric acid (SO_3)	0.008	0.009	0.008
	Phosphoric acid (P_2O_5)	0.13	0.09	0.06
	Lime (CaO)	0.013	0.014	0.004
	Magnesia (MgO)	0.02	0.019	0.008
	Potash (K_2O)	0.19	0.17	0.14
Total ash		0.41	0.29	0.24
Substances not determined (methyl-inositol)		1.66	0.83	0.86

SOLUBILITY OF RUBBER AND SO-CALLED "MODIFICATIONS"

Rubber dissolved in organic solvents is a lyophilic colloid. As dispersing media, chloroform, carbon tetrachloride, and carbon bisulfide are especially suitable. But many aromatic, hydro-aromatic, and aliphatic hydrocarbons may be used. If rubber is suspended in these solvents, it swells [38] more or

[31] Parkin, *Roy. Bot. Gard. Ceylon, Circ.*, **1**, 144 (1899).
[32] *Arch. Rubbercultuur*, **7**, 399 (1923).
[33] W. Gündel, *Sitzber. physik.-Med. Sozietät, Erlangen*, **60**, 248 (1928).
[34] *Biochem. J.*, **3**, 165 (1908).
[35] *Kolloid-Z.*, **12**, 147 (1913).
[36] F. Kaye, *India Rubber J.*, **45**, 1297 (1913); **48**, 165 (1914).
[37] *Kolloid-Z.*, **13**, 220 (1913); *Analyst*, **36**, 6 (1911).

* H. F. Bondy [*Ber.*, **66**, 1611 (1933)] has shown that the basic fraction of the acetone extract of rubber contains a naturally occurring colored substance which functions as an antioxidant in the latex. This colored substance presumably functions as a protective agent for the rubber, by absorbing the light of specific wave length, effective in promoting the auto-oxidation of rubber.

[38] E. Posnjak, *Kolloidchem. Beihefte*, **3**, 417 (1912); Spence and Kratz, *Kolloid-Z.*, **15**, 217 (1914).

less and gives with the aid of agitation the turbid-appearing dispersion generally known as rubber solution. In practice, very concentrated solutions (up to 1:4) for brushing purposes are prepared by stirring the rubber with solvents in the Werner-Pfleiderer machine. Many solvents, such as ether or petroleum ether, dissolve only a part of the rubber (see Fractional Solution of Rubber). The spontaneous solubility of non-milled Para rubber is very slight. Harries [39] states that about 1.2 to 1.4 grams of unmasticated rubber dissolve in a liter of benzene at room temperature. Exact figures in this connection are lacking. The solubility of a rubber sample depends entirely on its source and history. For example, mechanical treatment of rubber on the mill greatly influences its solubility. Rubber which has been freshly precipitated by adding alcohol to a rubber solution is readily soluble in ether. After standing for a short period, however, its solubility is decreased. Rubber is insoluble in alcohol, acetone, and acetic acid.

A strong Tyndall effect is exhibited by all rubber solutions in the rays of an arc lamp. Small oval light cones which show Brownian movement may be observed under the ultramicroscope.[40] Since the refractive indices of the dispersing and dispersed phases are almost identical, the investigation of highly dispersed rubber with an ultramicroscope is often very difficult. Staudinger [41] has expressed the opinion that all particles observed in rubber solutions with the ultramicroscope are due to impurities, and has been able to show that the colloidal particles of the purest synthetic isoprene rubber remained invisible with dark-field illumination.

Harries [42] has attempted to explain the varying solubilities of different samples of crude rubber by postulating so-called "modifications." He distinguishes between an ordinary, an insoluble, and an oily modification. The latter is formed when rubber solutions are kept at elevated temperatures for long periods. If the rubber in such a solution is precipitated with alcohol, there is no longer produced a semi-solid mass, but an oil.[43] After some time the oil again reverts to the normal form. The insoluble "modification" is produced on longer standing of precipitated rubber, and is especially predominant in Brazilian rubber that has been stored for a number of years. Milling, or heating with acetic acid, again converts it to the normal form.

Harries reported as a fourth "modification," the product obtained when he treated rubber with sulfuric acid. He believed this crumbly, insoluble mass to be a high-molecular weight polymer of rubber. Later Kirchhof [44] and also Staudinger [45] studied the action of sulfuric acid on rubber,* and they too found that the rubber was completely altered in physical and chemical properties by this treatment. They also showed that the new product had fewer double bonds than the original rubber. Kirchhof presumes that tetramethylene rings are formed at the expense of the double bonds. Staudinger calls the product cyclo-rubber, and thinks it is related to the substance that is produced when rubber is strongly heated (to about 300° C.). (*See* cyclization, p. 189). To what extent polymerization and depolymeriza-

[39] *Ber.*, **35**, 3261 (1902).
[40] Harries, Lecture at Vienna; Wo. Ostwald, *Kolloid-Z.*, **40**, 58 (1926).
[41] Address at Düsseldorf; *Ber.*, **59**, 3036 (1926).
[42] Harries, "Untersuchungen . . . . . ," p. 5.
[43] Pummerer and Burkard could not confirm this: *Ber.*, **55**, 3464 (1922). The "liquid rubber" dealt with by Harries was probably a decomposition product. We have observed that this occasionally occurring "liquid rubber" always contains some oxygen.
[44] *Kolloid-Z.*, **30**, 183 (1922).
[45] *Z. angew. Chem.*, **38**, 226 (1924).
* Translator's Note. Attention is called to the work of Fisher in this same field. H. L. Fisher, *Ind. Eng. Chem.*, **19**, 1328 (1927).

tion take place along with cyclization is not known. Tin tetrachloride seems to cause chiefly cyclization and polymerization.[46]

According to Harries, a fifth "stable modification" is present in vulcanized rubber (*see* p. 293).

The term "modification" for the various forms of rubber has been superseded, for today we know that we are dealing with various chemical and colloidal states of the same parent hydrocarbon or mixture of parent hydrocarbons. Harries proposed the term "aggregation" for the reversible association of true rubber molecules to form larger aggregates. Until a more complete knowledge of the mechanism of the reaction is obtained, aggregation, implying the reversible association of unsaturated molecules to particles of colloidal dimensions, must be considered quite distinct from polymerization, which refers to the process whereby the isoprene molecules combine through primary valences to form rubber molecules. The reverse of aggregation may, without causing confusion, be called "disaggregation." The term "disaggregation" is preferable to the looser name "dissociation."

Harries postulated for the fundamental rubber molecule a cyclic structure containing two isoprene groups (dimethylcyclo-octadiene). As late as 1915, he held to the idea that large rings containing 4 to 6 isoprene groups were the probable fundamental units. Harries' views have by no means been disproved. On the contrary, they now seem even more plausible, as will be seen later on. The open-chain formula for rubber has received much discussion, however, and the number of isoprene groups per unit molecule is now thought to be greater than Harries believed. Staudinger has quite a different concept. He postulates that the polymerization of isoprene produces directly so-called "macro-molecules." These are of colloidal size, have a molecular weight of about 100,000, and contain more than 1,000 isoprene groups. Staudinger [47] believes that these enormously long chains also exist in gutta-percha, polyformaldehyde, and polystyrene. This last named substance is the outstanding synthetic analog through which the structure of rubber may be investigated, just as polyformaldehyde is a synthetic substance having a structural pattern comparable to that of the thread-like cellulose molecule.[48]

Purification of the Rubber Hydrocarbon—The Problem of Crystallizing Rubber

Since the purity of the starting material is absolutely essential in exact chemical work, efforts have been made to prepare, by various means, the rubber hydrocarbon in pure form. Proteins, resins, and other organic substances associated with rubber are partly adsorbed and in the purification are retained with great tenacity by the rubber. Furthermore, rubber possesses the undesirable property of becoming more susceptible to oxidation as the purification and bleaching proceeds.[49] It is, therefore, not an easy matter to obtain the pure hydrocarbon, free from ash, oxygen and nitrogen. There are four distinctly different methods by which the rubber hydrocarbon may be purified.

[46] H. A. Bruson, L. B. Sebrell and W. C. Calvert, *Ind. Eng. Chem.*, **19**, 1033 (1927).

[47] *Ber.*, **62**, 241 (1929); *Z. angew. Chem.*, **42**, 37, 67 (1929).

[48] *Z. physik. Chem.*, **126**, 425 (1927).

[49] H. A. Bruson, L. B. Sebrell and W. W. Vogt, *Ind. Eng. Chem.*, **19**, 1187 (1927). These investigators have isolated from the acetone extract, substances, of the nature of sterols, which inhibit the oxidation of rubber.

Acetone Extraction

The first scientific method of purification—only such methods will be discussed—originated with Harries.[50] The procedure is as follows:

Crude rubber is suspended in benzene and allowed to stand for some time. Part of the rubber is thus dissolved. The solution is siphoned from the settlings and is then poured with stirring into an equal volume of alcohol. The alcohol precipitates the rubber, which is then extracted in a Soxhlet apparatus with acetone for 12 hours to remove the resins. The purpose of the precipitation from benzene solution, is to remove more of the soluble oxidation products, and to expose a fresh surface of rubber for the subsequent extraction. The operations of precipitation and acetone extraction are repeated as many times as desired (at least twice). An elementary analysis after the first extraction showed 86.30 per cent carbon and, according to Harries, this value rose after three reprecipitations to:

	C = 87.85%	H = 12.28%
Calcd. for $(C_5H_8)_x$	C = 87.15%	H = 11.85%

The product that Harries obtained in this manner was more or less colored, and had partially lost the characteristic elasticity of the crude rubber.

A similar method for preparing purified rubber was employed by Staudinger[51] in his early work. He made use of a procedure which was described by M. Wildermann.[52] To effect purification, the crude rubber is extracted with a solvent mixture, one ingredient of which is a solvent for the resins but not for the rubber, while the other is a solvent for both resins and rubber. With the use of such a mixture the rubber swells somewhat during the extraction and no longer holds the resins so tenaciously. The solvent mixtures utilized by Staudinger consisted of 80 to 40 per cent acetone and 20 to 60 per cent chloroform. This process is no longer used.

Fractional Precipitation

An essentially different method of purification was employed by Pummerer and Koch.[53] These investigators hoped to isolate a more soluble component of rubber by means of fractional precipitation. Thoroughly masticated rubber was extracted with acetone and then dissolved in benzene by allowing a mixture of rubber and benzene to stand for several weeks. To the solution which was decanted from the insoluble sediment, alcohol or acetone was added slowly, to precipitate the rubber fractionally. The first fraction included the oxidation products of the rubber, the inorganic constituents, and 30 to 40 per cent of the rubber. When further amounts of precipitant were added to the remaining "principal" solution a high grade product (Fraction 2) was obtained, the analysis of which checked very closely the calculated values for $(C_5H_8)_x$.

Calcd. for $(C_5H_8)_x$:	C = 88.15%	H = 11.85%
Found:	C = 88.1; 87.91; 88.2%	H = 11.75; 11.77; 11.92%

Though the original material was more or less colored, depending on its source, the final product was colorless. Inorganic substances could no

[50] Harries, "Untersuchungen . . . . p. 7.
[51] *Helv. Chim. Acta*, **5**, 795 (1922).
[52] *Chem. Zentr.*, **82**, I, 186 (1911); Ger. Pat., 229,386, Class 39b, December 13, 1910.
[53] *Ann.*, **438**, 294 (1924).

longer be detected, and the nitrogen content was very small. The fractional precipitation was carried out not only to purify the rubber but also to obtain fractions of the pure hydrocarbon of different solubility. It is very doubtful that the purified rubber is homogeneous in character. It is probable that we are dealing with a mixture of homologous hydrocarbons differing from each other in the size of the subscript x in their empirical formula $(C_5H_8)_x$, and also differing in their states of aggregation.

Pummerer and Miedel [54] directed further work on the purification of rubber toward perfecting the method of fractional precipitation. Complete absence of nitrogen must be obtained in order to prepare crystalline rubber, and also to hydrogenate rubber. Solutions similar to the "principal" solution mentioned above were further fractionated with various solvents. The scheme according to which these solutions were treated is as follows:

1. The solution is treated with the precipitant until it becomes turbid. In the course of several hours the mixture separates into two layers—a lower, concentrated solution and an upper dilute solution.
2. The separate solutions are then treated with an excess of the precipitant. A precipitate and mother liquor are obtained from each solution.

The precipitates are once more treated according to this scheme. Two things are accomplished by this procedure: In the first operation, the insoluble impurities are concentrated in the lower layer; while in the precipitation the oxygen-containing substances are left in the mother liquor.

The solvents, precipitating agents, concentrations, and temperature were varied in a series of fractionations carried out according to this procedure. Benzene, hexahydrotoluene, petroleum ether, and ether were used as solvents, and alcohol and acetone as precipitants. To modify the action of the alcohol, it was usually diluted with the solvent that was being used. The fractional precipitation, especially when benzene is employed, is usually accompanied by supersaturation phenomena. With only a slight variation in the amount of precipitant employed, the entire rubber content sometimes separates as a liquid phase of rubber and benzene. The quantity of precipitate is most easily regulated when petroleum ether is the solvent and acetone the precipitant.

Even so, this method did not produce the desired result. Products of a high degree of purity were obtained (they were soluble in hexahydrotoluene and partially in ether to form clear solutions) but the complete removal of nitrogenous compounds, essential for the preparation of derivatives, was not attained.

Midgely, Henne and Renoll* [*J. Am. Chem. Soc.*, **53**, 2733 (1931)], have succeeded in obtaining the rubber hydrocarbon, free from nitrogen, by a method of fractional precipitation with a mixture of benzene and absolute alcohol. This fractionation method was further applied to the rubber hydrocarbon itself [*J. Am. Chem. Soc.*, **54**, 3343 (1932)], in an attempt to separate the various components of the hydrocarbon. The progress of the fractionation was followed by measuring a "standard precipitation point" of the rubber solution. The standard precipitation point of a sample of rubber is defined as the temperature at which a sudden increase of turbidity occurs in a slowly cooled solution of 0.85 per cent rubber, 28.55 per cent absolute alcohol and 70.60 per cent benzene. The authors demonstrated that there is present in the rubber hydrocarbon a single component, amounting to more than 50 per cent and characterized by a standard precipitation point of 35° C. The same method has shown that milled rubber is made of a continuous series of undefined components, without a single predominating individual [*J. Am. Chem. Soc.*, 54, 3381 (1931); *J. Phys. Chem.*, **36**, 2880 (1932); *Rubber Chem. Tech.*, **6**, 367 (1933)].

[54] *Ber.*, **60**, 2149 (1927).

* Translator's Note.

Another method for the purification of rubber was recently reported by A. T. McPherson [*Bur. Standards J. Research*, **8**, 751 (1932)]. The purified rubber is prepared by digestion of crude rubber or latex at 190° C., followed by extraction with water and with alcohol, and drying in an atmosphere of inert gas. Rubber purified by this method contains about 99.5 per cent rubber hydrocarbon.

Crystalline Rubber

In 1924, Pummerer and Koch,[55] succeeded in isolating a crystalline fraction of rubber from the final mother liquor obtained in the fractional precipitation of rubber. White, tough, non-pulverizable spherulites formed in an oily precipitate that had stood for several weeks. In a melting-point tube, the crystals became transparent and isotropic at 60° to 62° C., and melted at 90° C. They could be recrystallized from ether, in which they were difficultly soluble in the cold and only slightly more soluble when warm.

On analysis, the following results were obtained:

Found:	C = 87.67%	H = 12.07%
Calcd. for $(C_5H_8)_n$	C = 88.15%	H = 11.85%

The product was extremely auto-oxidizable. On evaporation of its benzene solution, there remained on the watch glass a solid deposit composed of small spherulites which, when microscopically examined in polarized light, plainly showed double refraction. When the solid was fractured, its optical properties were retained. This observation was evidence for the fact that crystal aggregates were present. At present, little can be said concerning the crystallographic system to which the crystals belonged.[56] It would be a distinct advance for rubber research if it were possible to obtain in crystallized form the principal constituent of the natural rubber hydrocarbon in such quantity that it could be analyzed and its chemical constitution established. We are in no such fortunate position at present. Further experiments are being pursued with a view toward making possible the ready preparation of crystalline rubber by the cooling of rubber solutions as well as by the fractional solution of frozen rubber.

The isolation* of the rubber hydrocarbon in crystalline form has been accomplished at the Bureau of Standards, Washington, D. C. The crystals were obtained from a 0.05 per cent solution of purified rubber hydrocarbon in pure dry ether at —65° C. The melting point of the crystals lies between +9.5° and 11° C. The melted crystals are rubber-like in nature, and analysis indicates a hydrogen-carbon ratio of 8:5. The crystals were photographed at —50° C. [*Rubber Age (N. Y.)*, **28**, 79 (1930); *J. Franklin Inst.*, **210**, 5[illegible]; *Physical Review*, **38**, 1790 (1931); *Rubber Chem. Tech.*, **5**, 119 (1932); *Bur. Standards J. Research*, **10**, 479 (1933); *Rubber Chem. Tech.*, **6**, 351 (1933)]. Pummerer and Andriessen [*Kautschuk*, **5**, 133 (1929)] also observed that a 1 per cent solution of sol-rubber in ether solidifies at —70° C., but they failed to obtain the characteristic interferences of crystals, with the solid sol-rubber. Pummerer and v. Susich express the opinion that the solid phase is not crystalline rubber but rubber-ether gel [*Kautschuk*, **7**, 117 (1931); *Rubber Chem. Tech.*, **5**, 245 (1932)].

Shortly after the announcement of the investigation by Pummerer and Koch, the important observation was made by J. R. Katz and K. Bing[57] that all rubber elongated to 80 or 100 per cent or more gave an x-ray diffraction pattern typical of a fibrous structure. This behavior was predicted by L. Hock. From the intensity of the interference spots in the x-ray pattern, it is to be concluded that a considerable portion of the rubber hydrocarbon in elongated (by about 80 per cent) crude rubber is present in a crystalline form.

[55] *Ann.*, **438**, 300 (1924).
[56] Gross, R. *Ann.*, **438**, 311 (1924).
[57] *Z. angew. Chem.*, **38**, 439 (1925).
* Translator's Note.

Racked rubber, discovered by Feuchter,[58] is especially suitable in this method of investigation. The qualitative observations of Katz have been supplemented and quantitatively applied by Hauser and Mark,[59] and more recently by K. H. Meyer and Mark.[60] The presence of a considerable proportion of crystalline rubber hydrocarbon in crude rubber is not doubted by these authors. They explain the absence of interference spots in the case of unstretched rubber by assuming that the crystalline portion is swelled in the remainder. This fact could also be explained by assuming that rubber exists in a state similar to that of salt when the latter is just below its fusion temperature.[61] According to the measurements of Hauser and Mark, the simplest structural unit of crystallized rubber is relatively small. They assume that it contains eight isoprene groups. A relationship does not necessarily exist between the size of the unit structure and the size of the molecule.

From the length of the rubber crystallite (not the structural unit), Meyer and Mark have estimated the length of the isoprene chains as 75 to 150 isoprene groups; i. e., the number of groups connected by primary valences. Pummerer and Koch are of the opinion that primary valence chains of varying length, and containing less than 75 to 150 isoprene groups could not be detected by x-ray methods.[62] Incidentally they point out that the residual valence forces at the end of a chain are not of sufficient strength to hold together long molecules in the form of greater principal valence chains. It is to be noted that a third molecule acting as a link could fulfill this condition.

With the isoprene chains in such a parallel arrangement, the double bonds would have an orienting effect, and 1 and 2 would be held together by the valence forces of many pairs of adjacent double bonds in 1 and 3, and in 2 and 3.

A conclusion growing out of the theory of primary valence chains is that in stretched rubber, as well as in cellulose, topochemical reactions are possible, in which the fibre structure and its x-ray pattern remain almost unchanged. Neither Mark and v. Susich (loc. cit.) nor F. Kirchhof could detect the topochemical reactions in studying racked rubber.[63] The bromination of rubber produces a pseudomorph of the original bundle of fibres, which to outer appearances has remained intact, but no longer possesses a crystalline structure. The action of sulfuric acid on rubber (in the formation of cyclorubber) gives results which are more indefinite. The absence of topochemical reactions may also be due to the fact that the saturation of the double bonds results in very pronounced changes in the structure of the primary valence chains.

The thorough physical investigations of frozen raw rubber by A. van Rossem and J. Lotichius [64] are of great interest for the question of crystalline

[58] *Kautschuk*, **2**, 171, 197 (1926).
[59] Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 63 (1926); **23**, 64 (1926) (Ambronn-Festschrift). Stretched rubber has a number of interferences in common with crystallized rubber. The patterns are not identical, however.
[60] *Ber.*, **61**, 1939 (1928), more especially Mark and G. v. Susich, *Kolloid-Z.*, **46**, 11 (1928).
[61] Another very simple explanation, to which the authors take exception, was proposed by Wo. Ostwald. *Cf.* Wo. Ostwald, *Kolloid-Z.*, **40**, 58 (1926).
[62] In this connection compare a cellulose structure proposed by Staudinger. *Z. angew. Chem.*, **42**, 71 (1929).
[63] *Kautschuk*, **5**, 11 (1929).
[64] *Kautschuk*, **5**, 2 (1929).

rubber. The term "freezing" is applied to the phenomenon (long ago observed in commerce), which results in the rubber becoming hard and opaque on standing in a cold place for some time. On warming, the rubber "thaws" and becomes soft and elastic again. The authors referred to above compared the changes in specific gravity, hardness, and light absorption of a number of frozen rubbers at the temperature of thawing and demonstrated that in all cases the rubber suffers disruptive changes. The latent heat of fusion was also measured. All of the observed phenomena can be satisfactorily explained on the assumption that frozen rubber contains crystalline portions of rubber. The temperature at which the rubber thaws is referred to as the melting point. For rubber which had been kept frozen for about 10 years, the melting point lay between 35° and 37° C., and for rubber samples kept frozen for several years the melting point was between 31° and 33° C. This recalls to mind the rather sharp melting point (60° to 62° C.) of the crystalline rubber prepared by Pummerer and Koch. Rubber which has been thawed by warming and then rapidly cooled again, becomes turbid. The melting point of a sample thus treated is lower and less definite than that of a sample frozen for a long time. Several years before van Rossem's work, J. R. Katz [65] established proof that frozen rubber in the stretched condition exhibits the Debye-Scherrer x-ray pattern which disappears on thawing the rubber. Recent work by the same author [66] confirms and elaborates his earlier conclusions, which furnished the impulse for the work which was done in collaboration with van Rossem. Complete crystalline rubber was never obtained, since the characteristic ring of amorphous substances could always be recognized in the x-ray patterns of all samples.

In this connection, it is of interest to call attention to recent work of Katz [67] on the diameter of the amorphous rings which appear in the x-ray patterns of oils and stretched rubber. By means of the x-ray diffraction patterns, it is possible to distinguish between synthetic rubbers prepared from isoprene, methyl-isoprene, and butadiene.

Alkali Purification

Pummerer and Koch, for the purpose of obtaining pure rubber, combined another method with fractional precipitation. A solution of the purified "principal" fraction of rubber in petroleum ether was gently heated for several days on the water bath with a solution of potassium hydroxide in methyl alcohol.[68] In this process, as in the cold agitation of a rubber solution with a solution of potassium hydroxide in methyl alcohol (the cold treatment was an endeavor to protect the rubber as much as possible from decomposition) the last traces of protein and acidic substances can be removed. However, the subsequent complete removal of the alkali from the petroleum ether solution or emulsion, as well as the loss of rubber resulting from this treatment, makes this method seem practicable only when relatively small quantities of purified rubber are required.

Another method, related in principle to the above method, was therefore devised by Pummerer and Pahl. The order of operations, however, is reversed. They first treat preserved raw latex with an aqueous solution of alkali to remove the proteins. The purified rubber thus obtained is then fractionated. It should be possible in this way to decompose the protein which

[5] *Z. angew. Chem.*, **38**, 439 (1925).
[6] *Kautschuk*, **5**, 6 (1929).
[7] *Z. angew. Chem.*, **40**, 759 (1927).
[8] *Ann.*, **438**, 296 (1924).

is presumably adsorbed on the outer shell of the rubber globules in the latex suspension, even if this process is not practicable for commercial raw rubber. Furthermore, the resins which are not dissolved by the alkali can subsequently be removed with acetone. By using latex as the starting material, instead of commercial crude rubber with its widely varying and difficultly controllable properties, it was hoped to obtain quite uniform and definitely purified rubber. The latex used was from one to two years old and came from the *Hevea brasiliensis* plantations of Sumatra.

The protein of ammonia-preserved latex is only slowly attacked by cold alkali. The enzymatic removal of protein with trypsin had been tried by Freundlich and Hauser,[69] but had not been carried out quantitatively. They found a temperature of 37° C. suitable for the process.* Pummerer and Pahl were not successful in accomplishing the alkali degradation of the protein, either at this temperature or at the higher temperature of 45° C.; but at 50° C., the disappearance of the protein reaction in the presence of alkali could be followed over a period of several days. The purification with alkali is possible only because of the tendency of latex to cream when treated with alkali at 50° C. A hydrocarbon layer rises to the top while the brown alkaline water solution, which becomes yellow when the process is repeated, sinks to the bottom with the impurities. The water layer is drawn off, and the hydrocarbon layer is repurified several times with sodium hydroxide until the biuret and ninhydrin reactions disappear almost simultaneously. Most of the alkali which remains in the cream is removed by washing, and the last traces are removed by dialysis. The rubber is then coagulated and freed from water and traces of resins by warm extraction with acetone in a Soxhlet apparatus. This crude product is the *alkali-purified latex* which serves as a starting material for further experiments.

Since it was of special interest to know whether the difficultly soluble portions of the rubber were actually pure rubber or whether they contained oxygen, the whole purification process was repeated in a large round-bottomed flask in the presence of nitrogen. The product thus obtained was quite pure, but contained all of the difficultly soluble portions of the rubber exclusive of the proteins. It is debatable whether these difficultly soluble portions are actually rubber. In contrast to the individual components of the rubber, this purified product will hereafter be called *total rubber*. O. de Vries and N. Beumée-Nieuwland,[70] working with fresh latex, conducted similar experiments simultaneously with those of Pummerer and Pahl. According to them, fresh latex creams even when treated with cold alkali. Pummerer and Pahl could obtain no creaming with alkali in the cold when working with preserved latex. Even a lowering of the temperature of the experiment from 50° to 45° C. retarded the degradation of the protein. An exact comparison of the results obtained by Pummerer[71] on preserved latex with those obtained by O. de Vries and Beumée-Nieuwland on fresh latex, has been reported. The Dutch authors studied the behavior of rubber toward

[69] *Kolloid-Z.*, **36**, Zsigmondy-Festschrift, 21 (1925).

* Translator's Note. In the recent work of Smith, Saylor and Wing [*Bur. Standards J. Research*, **10**, 479 (1933); *Rubber Chem. Tech.*, **6**, 351, (1933)] on the crystallization of pure ether-soluble rubber hydrocarbon, these investigators utilized trypsin for the quantitative removal of protein from the rubber. Ammonia-preserved latex was dialyzed to remove ammonia. The protein was removed with trypsin in a 3 per cent solution of sodium bicarbonate at 38° C. Addition of sodium hydroxide to produce a 2 per cent solution caused creaming to take place at room temperature. Repeated creaming, followed by dialysis to remove alkali, yielded total rubber with a nitrogen content less than 0.02 per cent.

[70] *Arch. Rubbercultuur*, **9**, 714 (1925); *Chem. Abstracts*, **19**, 3615 (1925).

[71] R. Pummerer, *Kautschuk*, **2**, 86 (1926).

sodium hydroxide with the idea of preserving the rubber, and did not endeavor to obtain analytically pure samples. The very tacky or pitch-like consistency of the rubber obtained by them has no detrimental effect on the properties of the rubber if the alkali is thoroughly removed by dialysis, at least when the rubber is preserved in an atmosphere of carbon dioxide. In an experiment using crude methods of dialysis, the Dutch investigators obtained a stable and practically nitrogen-free product (0.02 per cent nitrogen).

Vacuum-dried total rubber obtained from preserved latex or Revertex, according to the directions of Pummerer and Pahl,[72] is transparent even in thick layers, somewhat yellow in color, and not tacky. The ash content of good samples is about 0.077 per cent, and the behavior of the total rubber toward vulcanization is normal.[73] The hard rubber prepared from it shows especially good insulating properties. There are no good reasons for believing that the 2 per cent sodium hydroxide solution has an effect on the rubber hydrocarbon at 50° C. Even the x-ray interferences characteristic for rubber were obtained by Hauser and Rosbaud with total rubber. On the other hand, the difference in behavior between fresh and ammonia-preserved latex when treated with alkali seems to indicate that the ammonia preservation of latex brings about some change. The time and manner of preservation are the most important factors in the latter case.

Procedure: A quantity of latex (e.g. 750 grams) preserved with ammonia and containing about 40 per cent by weight of rubber hydrocarbon, is agitated in the presence of nitrogen with an equal weight of 8 per cent sodium hydroxide solution, and is then diluted with distilled water (1250 cc.) until the alkali content of the suspension amounts to 2 per cent. The mixture is then stirred at 50° C. for two working days of from 8 to 10 hours, and at night is allowed to stand without stirring, at room temperature. The creaming takes place during the second night. The lower caustic layer is siphoned off, and the cream is subjected to the same treatment with alkali for another day. The creaming again takes place at night. The caustic layer is again separated, and the entire process is repeated three more times, although in the meantime the reactions for proteins and amino acids have usually disappeared. The permanganate reaction of the lower caustic layer must finally be negligible, so that the green manganate stage persists for several minutes in a very dilute solution. To obtain this test, as well as for the sake of the yield, it is essential to separate the suspended hydrocarbon from the lower caustic layer very thoroughly. Shortening of the process is possible, especially if the details of the procedure are very carefully observed. In order to protect the somewhat unstable hydrocarbon, it is desirable not to use higher temperatures or stronger alkali. When the above procedure is followed, the rubber of the preserved latex remains entirely unchanged.

The removal of the alkali by washing follows the major purification. The cream obtained according to the above directions is diluted with 2300 cc. of distilled water, and stirred at 50° C. for 8 hours. The cream is allowed to form and is then separated from the solution. Upon repeating the procedure, creaming sometimes fails to occur, and the cream from the first washing is therefore put into a dialyzer, e. g., Gutbier's dialyzer, [Mineralchemie A.-G., Oslau (Coburg)] of 1-liter capacity provided with a parchment membrane. In order to avoid coagulation, the cream is not stirred, but the parchment sack is allowed to rotate slowly. The distilled water used in the dialysis is renewed six times, at 3- to 5-hour intervals. With the use of the ordinary 20 per cent cream, the dialysis is continued until 1 cc. of the material inside the parchment requires 0.1 cc. of 0.02 *N* hydrochloric acid for neutralization. If it is desired to remove the alkali quantitatively, the cream must be diluted until it contains 10 per cent of the rubber hydrocarbon.

After dialysis, the rubber is coagulated by the addition of acetone or acetic acid. Acetone does not coagulate the rubber quantitatively, but it is suitable for preparing rubber for certain purposes, e.g., for optical measurements, in which the presence of hydrogen ions must be avoided. However, no variations in the properties of the rubber were noted when the coagulation was effected by acetic acid. The coagulated rubber is cut up into small pieces for the warm acetone extraction in the Soxhlet apparatus. In this case, the

[72] *Ber.*, **60**, 2149 (1927); *Kautschuk*, **2**, 85 (1926); *Rubber Chem. Tech.*, **1**, 163 (1928).

[73] Pummerer and Pahl, *Ber.*, **60**, 2162 (1927).

acetone extraction is essentially a drying process since the extract seldom contains resins. It appears, therefore, that the resins as well as the proteins are mainly adsorbed from the serum upon the surface of the rubber globules.[14] The resins which might be present on the inside of the globule could of course diffuse toward the surface of the globule, and could be dissolved there. It would be more difficult for the proteins to diffuse in a similar fashion.

As already mentioned, the degradation of protein in ammonia-preserved latex occurs only when the latex is treated with alkali at 50° C., while with fresh latex, the reaction proceeds in the cold. There also exists an additional difference in that alkali-purified rubber from ammonia-preserved latex always contains more nitrogen than the total rubber, prepared by alkali purification, from fresh latex or Revertex.

Nitrogen-Containing Impurities of Rubber. The total rubber obtained as above contains, according to the quality and the age of the latex sample, 0.1 to 0.4 per cent of nitrogen which cannot be removed by even the most thorough washing. This nitrogen was at first overlooked because it could not be detected in certain samples by qualitative Lassaigne tests, and because the determination of carbon and hydrogen in samples of total rubber by combustion without the use of a reduced copper spiral gave values which totaled 100 per cent. When a reduced copper spiral is used in the combustion tube, the sum of the carbon and hydrogen values is slightly less than 100 per cent. The direct nitrogen determinations were made according to Dumas' method, with samples weighing from 0.3 to 0.4 gram, or according to the Kjeldahl procedure, with 0.5 gram of substance. The latter method gave the lowest values. In many cases, the results of the two methods checked exactly, even when the nitrogen content was only 0.05 per cent. Usually the Dumas value was about 0.05 per cent higher, and occasionally the difference was even greater. In the Dumas method, the nitrogen is determined in a macro-combustion tube, although the best results are obtained if a micro-azotometer is used in the determination.

It is very noticeable that when samples containing 0.4 per cent nitrogen were analyzed by the Dumas method with the use of a reduced copper spiral, there was a deficit of not more than 0.4 per cent from 100 per cent in the carbon and hydrogen determinations. A substance with a protein-nitrogen content of 0.4 per cent would, because of the oxygen contained in the proteins, have to show a deficit of about 1 per cent in 100 per cent. These facts, together with the observation that in the alkali purification the protein reaction very shortly disappears, lead to the conclusion that the total rubber obtained by the alkali process is actually or almost totally free from proteins, and owes its nitrogen content to an amine formed by the action of ammonia on the latex during the preservation period. After continued boiling of benzene solutions of total rubber with water or sodium hydroxide solution, no substances which showed the biuret or the ninhydrin reaction were found in the aqueous solutions.

The supposition that preservation of latex with ammonia increases the nitrogen content of the total rubber obtained therefrom, was also substantiated by applying the alkali purification process to concentrated latex which was not preserved with ammonia. The usual Revertex produced by the Metallgesellschaft according to Hauser's process, or better still a special Revertex S (which after removal of the alkali by dialysis does not coagulate at the end of the process), gives a total rubber containing only 0.036 per cent nitrogen. It is not known whether this remaining nitrogen comes from the unattacked protein which is occluded in the small globules or whether it belongs to an

[14] *Cf.* H. Loewen, *Kautschuk*, **2**, 90 (1926) for a discussion of the rubber resins.

amine of high molecular weight. The results of these experiments with Revertex completely agree with the above-mentioned results of O. de Vries and N. Hermes-Nieuwland, who were able to purify fresh latex with cold sodium hydroxide solution until it contained only 0.02 per cent nitrogen.*

Fractional Solution of Raw Rubber

No reliable method has been found for removing the nitrogen-containing impurities from crude rubber by fractional precipitation with organic solvents (*see* p. 166). However, the reverse of this process (the fractional solution of raw rubber) accomplishes this objective. C. O. Weber,[75] in his experiments on the solubility of rubber, noticed that two phases were present in a solution of rubber in chloroform. Caspari [76] more thoroughly investigated the behavior of rubber in various solvents, and proved that a seemingly clear solution, as for example in benzene, contains some undissolved suspended matter. According to Harries, it is very essential in the purification of rubber by his method (*see* p. 166) that a preliminary settling of the portion insoluble in benzene be allowed to take place for several weeks. Caspari considered the insoluble substance to be similar to rubber, and concluded that rubber is not a uniform substance. The insoluble portion is transparent in benzene, and can be recognized therein only with difficulty, but when petroleum ether is added the benzene solution becomes turbid. Stevens,[77] who disagreed with Caspari's view, thought that a delayed rate of solubility was involved and that eventually all of the insoluble substances, except the protein, would go into solution.

Several years ago, Pummerer and Koch [78] pointed out the necessity of fractionating rubber to determine whether it is partly homogeneous or whether it is a mixture of isoprene polymers and associated polyprenes of different constitution. They found that the solubility of analytically pure rubber varies considerably in different solvents. For instance, rubber which forms a clear solution in benzene but gives a turbid solution in hexahydrotoluene and ether can be further purified to give a clear solution in hexahydrotoluene. After still further purification the rubber dissolves to a clear solution in ether. These differences in solubility could not be accounted for by the presence of oxygen-containing impurities, because the results of the analyses of all samples were always in agreement. For this reason, the term "purification" is no longer applicable to the separation of the insoluble hydrocarbons from the main portion of the rubber, when these hydrocarbons are intrinsic components of rubber. Analytical values no longer serve to characterize a pure rubber, but must be supplemented by consideration of the previous history, the unsaturation (iodine or oxygen titer), the behavior, and the viscosity of the rubber.

Feuchter [79] has recently studied the fractionation of rubber and repeated the work of Caspari. He confirmed the fact that a difficultly soluble portion of the rubber remains after treatment with various solvents, especially ether and petroleum ether. Feuchter isolated about 78 to 82 per cent of the prin-

* Translator's Note. Cummings and Sebrell, [*Ind. Eng. Chem.*, **21**, 554 (1929)] using 30 per cent ammonia-preserved latex, extended the method of Pummerer and Pahl (treatment with 2 per cent sodium hydroxide solution) to include six changes of alkali. The purified rubber thus obtained contained from 0.004 to 0.009 per cent nitrogen. After further extraction of the purified rubber with acetone, the nitrogen content was reduced to so low a value that it could not be accurately determined by the colorimetric method with Nessler's solution.

[75] *Ber.*, **33**, 779 (1900).
[76] *J. Soc. Chem. Ind.*, **32**, 1041 (1913).
[77] *J. Soc. Chem. Ind.*, **38**, 192 T (1919).
[78] *Ann.*, **438**, 294, 297 (1924).
[79] *Kolloidchem. Beihefte*, **20**, 434 (1925).

cipal soluble portion, which he called "diffusion rubber," and showed that it possessed the most important properties of rubber. The insoluble portion, which contained all of the impurities, the protein, the sugars, etc., he called the "gel-skeleton" and considered that it contributed nothing to the elastic properties of rubber. Because of its impurity, the chemical nature of the insoluble portion has not been determined. The types of these impurities make it appear probable that they are the foreign substances of rubber, along with some adsorbed rubber. This is a view similar to that expressed by Spence and by Feuchter. The nature of the hydrocarbon contained in the principal insoluble portion was not established by the authors just mentioned.

By observing certain definite precautions and using ether or petroleum ether as the solvent, it is possible to obtain by Feuchter's method a "diffusion rubber" almost free from nitrogen. The best results are obtained by the use of coagulated raw latex or coagulated purified latex which has not been milled. The results are less satisfactory when the method is applied to smoked sheets. Sheet and crepe rubber receive more or less milling on the plantation, (*see* p. 112 ff.) and thus the structure of the latex globules is partly destroyed. More difficulty is therefore experienced in separating the insoluble portion, which according to Freundlich and Hauser [80] is probably the firm "hull substance" of the globules in the latex. With smoked sheets, the gel-skeleton has been disintegrated and is distributed in the solution in the form of fine fibers. It is then difficult to decant from the undissolved material, and difficulties arise similar to those encountered in the fractional precipitation of rubber.

In order to remove water-soluble compounds, salts, carbohydrates, etc., from rubber, it is best to dialyze preserved raw latex or diluted Revertex S and then to coagulate it and remove the admixed resinous impurities by an acetone extraction of the coagulum in the Soxhlet apparatus. This rubber, when dried and cut into small pieces, dissolves in ether to give a solution of very pure "diffusion rubber." Very pure fractions of rubber can also be obtained from sheet and crepe rubber by continuous extraction with ether, according to the method described below. The entire mass cannot be purified in this manner, however. Especially the ether-insoluble portion (the rubber-like nature of which is debatable), does not lend itself to this purification, since all of the impurities of the rubber, especially the proteins, are concentrated in this portion. The ether-soluble portion may contain up to one-fourth of its weight of foreign substances. By fractional solution of alkali-purified total rubber (*see* p. 170), Pummerer and Pahl obtained an insoluble portion which resembled the above ether-insoluble portion.

Sol- and Gel-Rubber. We are indebted to Freundlich and Hauser [81] for the fundamental microscopic proof that the globules in latex, which was investigated in the tropics, consist of viscous interiors surrounded by solid elastic skins, which when punctured allow the viscous contents to escape. Their work shows definitely that there are two phases of rubber, provided of course that the outer layer is actually rubber and not perhaps a mixture of rubber, resins, and proteins. The above authors assumed that the "hull substance" consists of rubber, but do not give further analytical proof for the statement. With this important evidence for the two-phase theory, the purification and fractionation of rubber must be considered by far the most important problem for the chemist interested in the preparation of derivatives

[80] *Kolloid-Z.*, Zsigmondy-Festschrift, Supplement **36**, 15 ff. (1925).

[81] *Kolloid-Z.*, Zsigmondy-Festschrift, Supplement **36**, 15 ff. (1925).

of rubber. In the present state of rubber research, one would not think of ozonizing such a crude mixture as raw rubber, or in any other way endeavoring to determine its constitution. Of course, the fundamental importance of Harries' earlier work on the ozonization of rubber for the purpose of determining the structure of the rubber molecule cannot be discredited. Even in the ozonization of crude rubber, the loss of over 20 per cent of the original material is difficult to explain.

Pummerer and Pahl, using total rubber in their experiments, directly attacked the fundamental colloid chemical problem of the two phases of rubber. When the ether-soluble portion, called "sol-rubber,"[82] is extracted from finely cut rubber, there remains, depending upon the previous treatment, from 20 to 45 per cent of a more difficultly soluble portion in the form of swollen gelatinous pieces. On drying, these pieces prove to be rubber $(C_5H_8)_x$, containing a trace of ash (about 0.2 per cent) and some nitrogen. The nitrogen is presumably not protein nitrogen. It had been possible before this work to decrease the nitrogen content to about 0.017 per cent, but more recently with unprecipitated gel from Revertex S, the nitrogen content has been decreased to a value as low as 0.004 per cent.

The new ether-insoluble component has been given the name "gel-rubber." This insoluble portion of the rubber undoubtedly contains the "hull substance," previously isolated from the latex particles by Freundlich and Hauser. In addition the gel-rubber also contains a considerable amount of "hull" components which were dissolved in the interior fluid (the interior fluid is for the most part sol-rubber). Sol- and gel-rubber differ primarily in that the former is pure white and very elastic, while the gel-rubber, before it is again dissolved, is brown and very tough. The softening temperature of sol-rubber lies between 115° and 130° C., and that of gel-rubber between 145° and 160° C. Total rubber, the purified starting material, softens at 130° to 145° C. At the first temperature given in each case, the contours of the individual rubber fibers begin to disappear when heated in a tube, while at the second temperature they are no longer discernible.

Proof for the logical assumption that in gel-rubber the crystallized portion, and therefore the difficultly soluble portion, predominates, has not yet been obtained. Hauser and Rosbaud conducted comparative x-ray investigations on sol- and gel-rubber. With sol-rubber, extension to the point where interferences appear is very seldom possible immediately after it is prepared, because the rubber, which comprises a colloid chemical system characterized by great elasticity and toughness, has been separated into an elastic (sol) and a tough (gel) component. After standing for several weeks with exclusion of air, sol-rubber is more extensible than when first prepared.[83] Interferences which are just as strong as those in ordinary crude rubber appear in both components of rubber before and after vulcanization insofar as the same degree of stretching is possible. Preliminary results on the vulcanization of pure rubber, sol-rubber, and gel-rubber have also been reported.[84] Previous experiments on the hot vulcanization of total rubber show that it is vulcanized considerably more rapidly than the two components separately.

[82] This portion is nothing but an especially pure form of Fenchter's "diffusion rubber," obtained from acetone-purified total rubber.

[83] Although this fraction remains ether-soluble at room temperature, the first sign of aggregation or orientation of the molecules can be recognized.

[84] Pummerer and Pahl, *Ber.*, **60**, 2162 (1927); *Rubber Chem. Tech.*, **1**, 167 (1928).

A continuous process devised by Pummerer, Andriessen, and Gündel,[85] for obtaining sol- and gel-rubber by the fractional solution of the most diverse raw rubbers, is described in the following section. Naturally, no quantitative separation of the various hydrocarbon types is accomplished, but the method represents a step in this direction. In order to simplify the work with samples of rubber which have been treated in different ways, the method will be described in detail.

In this connection it should be remarked that, according to a process developed by R. Pummerer, H. Kroepelin, and H. Miedel, it is possible to dissolve gel-rubber very rapidly and easily in organic solvents, if small quantities of bases (ammonia, amines of the aliphatic series, or piperidine) or acids (acetic, brombenzoic, and others) are added to these solvents. By this procedure, chemical action is not at all precluded. In the case of trichloracetic acid, a slight decrease in unsaturation has in fact been determined, by titration with iodine chloride.[86]

The Fractional Extraction of Latex and of Crude Rubber with Ether. This investigation, which, in contrast to Feuchter's diffusion method, takes place as a continuous fractionation in a current of ether, has the following objectives:

1. To investigate various rubber preparations under similar conditions as to their sol-rubber content.
2. To determine the effect of various treatments preliminary to extraction (sodium hydroxide, acetone extraction, heat).
3. To obtain pure fractions from different crude rubber types for the purpose of analytical investigation.
4. To effect the extraction of rubber with ether more rapidly and more completely.

For the fractionation of rubber, the overflow extractor shown in Figure 45 is used. The flask *A* has a capacity of 1.5 liters and is provided with a

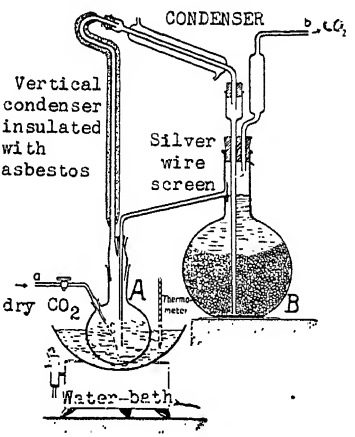


Figure 45—
Continuous extraction apparatus.

ground glass joint. Several flasks are used for changing the liquid during the extraction. Dry ether is placed in flask *A* and the ether is boiled vigorously by heating on a water-bath kept at 50° to 60° C. by means of an electric hot plate. The vapors ascend through a tube insulated with asbestos paper and are condensed at such a rate that a thin stream of ether flows through the vertical tube to the bottom of the large flask *B* (3.5 liters). Here the rub-

[85] *Ber.*, **61**, 1583 (1928); *Rubber Chem. Tech.*, **2**, 367 (1929).

[86] Fisher and Gray, *Ind. Eng. Chem.*, **18**, 414 (1926).

ber is extracted by the ether, and the solution then flows in a continuous stream through the overflow tube back into flask *A*. To prevent the carrying over of fragments of gel-rubber, the mouth of the overflow tube is provided with a fine-mesh silver-plated copper screen (such as is usually used for spirals). A few centimeters above the level of overflow there is a small hole in the vertical tube for the escape at *b* of dry carbon dioxide (air-free) which enters flask *A* at *a*. From here the gas passes through an empty flask and a mercury valve to prevent air from entering the apparatus as a result of pressure variations or interruptions. The introduction of carbon dioxide prevents delay of boiling in *A* and protects the rubber from oxidation. The apparatus is large enough to extract 100 grams of rubber. About two hours are required for the circulation of the ether through the system.

A "fraction" is understood to mean the quantity of rubber extracted in 24 hours. The first fraction, however, is removed after 6 hours, since in the beginning a relatively large quantity of rubber is dissolved and the solution in *A* may become too viscous. To isolate the rubber, the flask *A* is removed (another being put in its place), most of the ether in the flask is evaporated at 45° C. in a current of carbon dioxide, and the residue is dried under high vacuum at 45° C. The rubber is then preserved in an atmosphere of carbon dioxide.[87]

The following varieties of rubber were continuously extracted in the above apparatus: (1) purified "total rubber" obtained from preserved latex by the sodium hydroxide method of Pummerer and Pahl; (2) dialyzed ammonia-preserved raw latex (from plantation *Hevea brasiliensis*); (3) crepe; and (4) smoked sheets. The last two were extracted with acetone. When using acetone-extracted smoked sheets, the ether had to be boiled more slowly because of the danger of disintegration of the rubber. This accounts for the abnormally slow rise of the curve for smoked sheets in Figure 46.

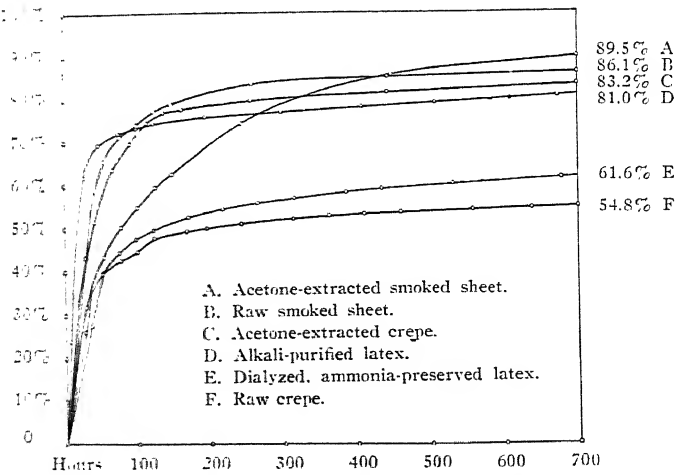


Figure 46—Continuous extraction of rubber.

[87] If in some cases it is not desired to boil the ether solution of rubber in *A* for such a long time, the solution may be continuously siphoned from *A* into an evaporating flask. The evaporated ether must then be returned to flask *B*.

Figure 46 shows the results of these experiments, the abscissa representing the time (in hours) of extraction, and the ordinate the percentage of the original rubber dissolved by the ether. The rubbers used in the ether extraction were previously extracted with warm acetone.

Total Rubber. By allowing smoked sheets to stand in ether, with frequent renewal of the solvent, according to Feuchter's process, Pummerer and Pahl [88] separated their total rubber into sol- and gel-rubber, 35 per cent of gel-rubber being obtained in one case.

When the rubber was subjected to continuous extraction for 40 hours (at the end of which time 65 to 70 per cent of the total rubber was dissolved) a distinct break in the curve occurred. Beyond this point, relatively little rubber was dissolved; namely, only about 0.2 to 0.3 per cent of the original amount for each 24 hours thereafter. The residue, as well as the traces of rubber which are extracted in the final fractions, can be considered as gel-rubber. From the tenth to the thirtieth day of extraction, the solubility of the residue remains approximately the same, and the gel-rubber is therefore considered to be fairly homogeneous. The solubility of total rubber is not determined, but only its rate of solution. Further fractionation experiments on the main portion of gel-rubber are recorded below. The small quantities of rubber which are dissolved in the fractions subsequent to the time represented by the break in the curve are known to be gel-rubber because, unlike the rubber isolated from the first four fractions (sol-rubber), the rubber obtained from the last fractions dissolves much more slowly in ether, and on standing becomes insoluble in ether.

Alkali-purified rubber, before coagulation, is also soluble in certain solvents and can be fractionated. The fractionation is best accomplished by the method of Miedel, in which a second solvent (acetone) is added to the solvent for the rubber (hexahydrotoluene), for the purpose of wetting the hydrocarbon particles. For example, 1 cc. of purified latex, containing 10 per cent of rubber, is treated with 30 cc. of a mixture of hexahydrotoluene and acetone (equal volumes). A considerable portion (52 to 55 per cent) remains undissolved, while the sol-rubber (45 to 48 per cent) dissolves and can be isolated from the hexahydrotoluene solution. The acetone is first removed from the hexahydrotoluene solution by shaking it repeatedly with water, separating the two layers, and drying the hexahydrotoluene solution. The portion of the rubber which is insoluble in the mixture of hexahydrotoluene and acetone is in this case not pure gel-rubber, but still contains sol-rubber, since the mixture of hexahydrotoluene, acetone and water does not dissolve sol-rubber readily.

However, the experiment shows that the insoluble component is present before coagulation. Even unpurified preserved latex, which yields the rubber hydrocarbon exceedingly slowly to the ordinary organic solvents such as benzene, can be dissolved in hexahydrotoluene-acetone. The rubber globules in this case still retain the protein shell and therefore dissolve less readily than the rubber of alkali-purified latex.

Ammonia-Preserved Latex. Ammonia-preserved latex which was used in the alkali-purification method, is also used for the ether extraction. After being freed from water-soluble substances by dialysis, the latex is coagulated, and extracted with acetone. The curve for the extraction with ether of this product, which still contains all of the protein, rises much more slowly, and

[88] *Ber.*, **60**, 2151 (1927).

even after 850 hours this rubber yields less extract than does total rubber after only 50 hours. In this case too, a break in the curve is evident, although less pronounced. If unpurified latex, which has been coagulated and exhaustively extracted with cold acetone, is extracted with ether, only a few per cent of the sol-rubber is dissolved by the ether, presumably because the protein shell of the globules is still present.

Para Crepe. (a) The course of the curve of extraction of a raw Para crepe (*see* p. 178) is strikingly similar to that of ammonia-preserved latex treated as described above. The extraction proceeds rather slowly, and the break in the curve is evident as before. It is surprising that after 52 per cent has been extracted, only very small quantities are dissolved. The crepe therefore contained 48 per cent gel-skeleton.

(b) Repetition of the experiments, using the same crepe except that in this case it had been previously extracted with acetone, showed far different results. When freshly extracted with acetone and dried in high vacuum, the crepe was quite unsuitable for fractionation with ether, because it swelled very rapidly and disintegrated into minute flakes, which were not retained by the silvered copper screen. However, after this crepe had stood for three months under carbon dioxide, this difficulty was overcome, and the sol-rubber was then extracted by the ether more quickly and in greater quantity than before storing. After 45 hours, 55 per cent had gone into solution, and after 150 hours, an equilibrium was reached at which but little more dissolved. The residue of gel-skeleton after 700 hours amounted to 16.8 per cent of the original material. The ether extraction of acetone-extracted crepe, which had been stored for 1½ years after the acetone extraction, resulted in a larger residue of gel-skeleton, namely, 28.1 per cent. After storage of crepe, which had been disaggregated by treatment with warm acetone, the solubility had considerably decreased.[89]

The continuous ether extraction also permitted the preparation in a convenient way of analytically pure sol-rubber from crepe. With acetone-extracted crepe, the first fraction was colorless and almost nitrogen-free, and had a composition corresponding to the following analytical values:

Wt. of sample for combustion 0.1338 gram; CO_2 0.4326 gram; H 0.1428 gram. Per cent C, 88.18; H, 11.94. With raw crepe, a product of this purity was first obtained in the third fraction. The fractions beyond the ninth one were no longer analytically pure, probably because of contamination with fibers resulting from the slight disintegration of the gel-skeleton. The tenth fraction, for example, showed the following percentage analysis: C, 87.74; H, 11.75, and contained more nitrogen than the lower fractions. The increase in the nitrogen content with the number of the fraction is illustrated by the following series of nitrogen determinations (Dumas method):

Fraction 1	0.055%	Fraction 7	0.33%
Fraction 3	0.13 %	Fraction 9	0.46%
Fraction 5	0.20 %	Fraction 10	0.50%

The gel-skeleton remaining after extraction showed the following percentage analysis: C, 81.35; H, 11.06; N, 2.06; Ash, 1.02; O (by difference), 4.51. From this analysis, the protein content of the gel-skeleton of crepe is calculated to be about 13 per cent. To obtain pure gel-rubber from crepe, the gel-skeleton was allowed to swell in benzene for six weeks. The clear solu-

[89] Changes at the protein-rubber interface can also play a part in this case. The abnormally low sol-rubber values which are obtained with unpurified latex (*see* above) but not with acetone-extracted crepe, are also probably influenced by this factor to some extent.

tion of benzene above the flakes was siphoned off, the benzene was evaporated *in vacuo* and the residue was dried in high vacuum at 50° C. The remaining gel-rubber was pale yellow in color and tough, and gave the following values on analysis:

Substance, 0.2181 gram. N, 0.3 cc. (15.5° C., 733.5 mm.)
Substance, 0.1284 gram. CO_2, 0.4154 gram; H_2O, 0.1363 gram

Calcd. for $(C_5H_8)_x$: C, 88.15; H, 11.85. Found: C, 88.23; H, 11.88; N, 0.15

The carbon and hydrogen determination in this case was carried out without the use of a reduced copper spiral. When this gel-rubber was kept in a 2 per cent benzene solution for several weeks, it yielded a highly viscous gel, while the second fraction of the sol-rubber, with about the same nitrogen content (about 0.1 per cent) gave a true, although viscous, solution. The value for the relative viscosity of gel-rubber, in 1 per cent benzene solution, was about three times the value obtained with sol-rubber (about 18 to 6).

A further removal of the nitrogen-containing impurities in undissolved gel-rubber seems possible by redissolving the freshly prepared samples in petroleum ether. For the sake of completeness, the analysis of the crepe investigated is given: 3.5 per cent of water and resin were extracted by acetone, while the dried residue contained C, 87.27; H, 11.88; N, 0.57 (Dumas) and 0.37 (Kjeldahl); Ash, 0.22.

To explain the notable effect of acetone extraction on crepe, which was manifested in an increased sol-rubber content, a study was made to determine whether this effect was thermal or whether it was the result of preliminary swelling in the acetone.

Five grams of finely divided crude crepe were sealed under carbon dioxide and warmed at 60° C. for six days. Another sample of five grams of finely divided crepe was digested in acetone at room temperature for six days, and the rubber was then isolated. Both samples, together with a control sample of untreated crepe, were then digested with enough ether to make 1 per cent solutions. These solutions were agitated for a short time twice daily, and after six days the solutions of sol-rubber were poured off from the insoluble part and washed. The sample which had been warmed gave a highly fibrous residue and a turbid solution. The sample treated with acetone exhibited a similar behavior but to a lesser degree. In the first case, 82.3 per cent of sol-rubber was extracted; in the second case, 56.7 per cent; from the untreated control sample, only 40 per cent. The action of boiling acetone on crepe rubber during extraction is chiefly thermal. The swelling effect, which was measured at room temperature instead of at 56° C., the boiling point of acetone, was actually too small.

The gel-skeleton from unextracted crepe (40 per cent yield) was kept in carbon dioxide in a sealed tube for one year, and was then digested with ether. The amount of rubber which was now extracted with ether was 4.6 per cent more than should have dissolved according to the extraction curve of the gel-skeleton for the previous year. Therefore, on standing, ether-soluble sol-rubber was again formed from the gel-skeleton. After warming at 60° to 65° C. for 30 days, this same gel-skeleton contained 27.5 per cent sol-rubber.

Smoked Sheets. Smoked sheets, when digested in ether with repeated shaking (according to Feuchter's method), do not give clear ether solutions, and the sol-fractions contain nitrogen. However, the continuous extraction, with careful manipulation, gives very good results with this rubber. The

sol-rubber dissolved very rapidly, the curves showing a pronounced break after 60 to 70 hours, when 70 per cent had been extracted. The ultimate value after 700 hours was 86 per cent sol-rubber. The high sol-rubber value obtained for smoked sheets is to be ascribed to the fact that in the smoking process the rubber is warmed at 45° to 50° C. for six to ten days.

Both initial fractions, which were of amber color in the case of unextracted crepe, were in these latter cases an intense orange color. The analysis of the third fraction, which was colorless and practically nitrogen-free, gave the following values: C, 88.17; H, 11.84 (a pure product). The values for the viscosities of solutions of these sol-rubbers are of the same magnitude as those for solutions of sol-rubber from crepe. The later fractions in this case also contained somewhat more nitrogen. Fractions 1, 3, 5, 7, 9 and 10 showed the following nitrogen values (Dumas method): 0.06, 0.14, 0.13, 0.15, 0.25, 0.34. The ether was decanted as slowly as possible, in order to prevent fibrous material from being stirred up into suspension. When the procedure was carried out rapidly, the last fractions contained 0.7 per cent nitrogen.

The gel-skeleton from smoked sheets (13 per cent by weight of the original material) gave the following analytical values: C, 77.89; H, 10.90; N, 3.25; Ash, 1.91; O (by difference), 6.04. From this analysis the protein content is calculated to be 20.4 per cent. The smoked sheets, after extraction of 3.4 per cent of water and resin by acetone, gave the following analytical values: C, 87.02; H, 11.98; N, 0.46 (Kjeldahl), 0.65 (Dumas); Ash, 0.3.

The Mutual Transformation of Sol- and Gel-, and of *Alpha*- and *Beta*- Rubber

The mutual transformations between ether-soluble and ether-insoluble rubber, which have been observed by technologists for decades, have only in recent years been the object of more exact scientific investigation. Pummerer[40] pointed out that the first fractions of sol-rubber, when preserved for one year in a sealed tube from which air was excluded, remained completely ether-soluble, while under the same conditions very slow formation of gel-rubber occurred in fractions beyond the fourth or fifth. The fractions of sol-rubber above the fourth, as we now know, show a higher nitrogen content than the first fractions, and it is therefore possible that some of the gel-rubber from the insoluble portion has passed into these fractions during extraction with the ether.

Gel-rubber which has been reprecipitated from benzene solution with alcohol also becomes partly insoluble in ether on standing, although it is originally completely soluble in ether. The insoluble gel-rubber which is again formed on standing, is, however, never as insoluble in ether as the gel-rubber when first obtained, for example, from total rubber. Even reprecipitated gel-rubber usually contains about 0.15 per cent of nitrogen and requires several weeks for solution in ether, while sol-rubber with a nitrogen content of 0.1 to 0.2 per cent is dissolved in 24 hours and forms a solution which never becomes turbid. After a sample of reprecipitated gel-rubber (obtained from Revertex), containing only 0.04 per cent nitrogen, had been stored for three months it dissolved completely in ether after three days although the gel-rubber, in contrast to sol-rubber, had not at first formed transparent, swollen gel-crumbs.

Experiments on the determination of the iodine number of rubber (*see* p. 197) have shown that gel-rubber exhibits a chemical behavior toward

[40] Address, delivered at Essen; *Kautschuk*, **3**, 234 (1927).

iodine chloride which is different from that of sol-rubber. The problem is therefore more complicated than was assumed by earlier investigators. In the first place, a minimal nitrogen content is of great importance for the formation of an ether-insoluble phase in rubber, although this phase later consists of almost 100 per cent gel-rubber. Secondly, the chemical component, gel-rubber, when freshly prepared, is soluble in ether, as is sol-rubber, but on standing becomes more difficultly soluble, and on going into solution first becomes turbid.

In 1927, Paul Bary and E. Fleurent [91] studied the change in the degree of polymerization of rubber. Ceylon *Hevea* sheets freshly prepared in 1914 were completely soluble. After storage in the dark until 1927, these sheets were partly soluble: smoked sheet was 22.5 per cent insoluble in benzene, and 23.8 per cent insoluble in ether; crepe was 15.6 per cent insoluble in benzene, and 20 per cent insoluble in ether. Moreover, a block of Para, after being stored for 75 hours at 52° C., showed considerably more of the soluble component in cold benzene in 56 days than originally. (*See* p. 181 concerning the formation of ether-soluble components from gel-skeleton on standing.)

P. Bary and E. A. Hauser,[92] in a joint communication on "Researches on the Structure of Rubber," have reviewed the reversible change of soluble rubber (called *alpha*-rubber) to insoluble rubber (called *beta*-rubber). They assume that an equilibrium exists which can be displaced by heat and mechanical treatment. The *beta*-rubber is distinguished from the *alpha*-rubber solely by its higher degree of polymerization, or more correctly, degree of aggregation. Since gel-rubber exhibits a chemical behavior different from that of sol-rubber, it is difficult to assume an equilibrium between the two forms if one does not wish to ascribe to the micelle a fundamentally different mode of reaction. Gel-rubber could, however, exist in an ether-soluble *alpha* form and an ether-insoluble *beta* form, and these two could be in equilibrium with each other. That the gel-rubber after preparation no longer contains appreciable quantities of sol-rubber, is also shown by the concordant iodine numbers of gel-rubbers from various sources. However, it is not known how much *alpha*-gel-rubber exists in sol-rubber. It is possible that the re-formation of the ether-insoluble *beta*-gel-rubber is connected with a certain swelling value of *alpha*-gel-rubber in sol-rubber, which value is only reached in later fractions. If this is the case, it is entirely possible that an *alpha*- and a *beta*-form exist in sol-rubber. Both would be ether-soluble, but could be distinguished by their extensibility and heat of swelling (*see* p. 478).

Just how the *alpha* and *beta* forms are to be visualized is not yet clear, but will probably be determined by following the changes on aging, and by applying titrometric and viscosimetric methods. There are two possibilities:

1. It may be that we are actually dealing with polymerization through primary valences—a continuation of rubber synthesis. If this proceeds by the union of isoprene groups, a large number of unit rubber molecules would be formed (polymerization of the first degree, irreversible at room temperatures and slightly above, in which each homolog differs from the adjacent members of the series by the C_5H_8 group). These polymers could then probably react further to produce more complicated structures by the union of two or more unit molecules (polymerization of the second and higher orders, slowly reversible at room temperature and quite readily reversible at slightly elevated

[91] *Compt. rend.*, **184**, 947 (1927); see also P. Bary, *Rev. gen. caoutchouc*, **4**, No. 31, 3 (1927).

[92] *Kautschuk*, **4**, 96 (1928); *Rev. gen. caoutchouc*, **5**, No. 42, 3 (1928); *Rubber Age (N. Y.)*, **23**, 685 (1928).

temperatures[4]. This could also be pictured by assuming the disappearance of double bonds through the formation of four-membered rings. Continuation of the same fundamental type of polymerization of the first order with the formation of long chains, would involve the assumption of low molecular velocities in the case of the larger molecules and the presence of isoprene in the system.

2. It may be that polymerization by addition to produce more complex polymers proceeds through secondary valences, or generally through van der Waal's forces, and is to be designated as association or aggregation. In general, association at a given temperature proceeds rapidly. In the case of rubber, because of the sluggish nature of the system, the process may be checked. Benzoic acid, when dissolved in benzene, is at once present in the di-molecular form; and carbon tetrachloride, when dissolved in cyclohexane, immediately forms aggregates consisting of four molecules of carbon tetrachloride.[93] In the colloid chemical system of rubber, however, no such free mobility of the particles may be assumed, and the orientation, as well as crystallization, may therefore require a long time. The gelling of a solution can probably be considered as a phenomenon parallel to that mentioned in this paragraph.

The beginning of the reversible *alpha-beta* equilibrium could itself be accelerated by warming, if in so doing the complex *beta*-system is not thermally degraded. In this connection, the following experiment of Kroepelin and W. Brumshagen[94] is of great interest. If freshly prepared alkali-purified sol-rubber which shows no structural viscosity and is composed essentially of *alpha* types of sol- and gel-rubber is heated for five days in a closed tube at 60° C. under carbon dioxide, the viscosity increases about 1.5 times, and in addition there appear anomalies (structural viscosity). If the experiment is continued for twenty days instead of five days, the result is the same. This shows that after five days an association equilibrium has been reached. If this is a true polymerization, it is hard to understand why the process does not continue. It is highly improbable that a thermal polymerization equilibrium is reached after so short a time. In this experiment, the rubber used is ether-soluble both before and after treatment.

Behavior of Rubber on Heating

The Dry Distillation of Rubber

At a comparatively early time attempts were made to deduce the structure of the rubber hydrocarbon from a study of the products obtained by the pyrogenetic decomposition of rubber.[95] Purified natural rubber, when heated in air,[96] begins to soften at 120° C., and as the temperature is increased, changes to a thick brown oil, which does not solidify or become elastic again and which has lost its typical rubber-like properties. At about 300° C., cracking takes place and a large number of decomposition products are formed, the boiling ranges of which lie between 180° C. and 300° C.

The first important attempt to distil rubber at atmospheric pressure was made by Himly.[97] He described two products resulting from the distillation:

[3] Scheibe and Felger, Dissertation of E. Felger, Erlangen, p. 59, **1926.**

[4] Dissertation of Brumshagen, Erlangen, **1929.**

[5] Ditmar, "Der pyrogene Zerfall des Kautschuks," Steinkopff and Springer, **1907.**

[6] Rubber is much more stable to increasing temperature when heated *in vacuo* or in inert gases.

[97] "De Caoutchouk ejusque destillationis siccae productis et ex his de Caoutchino, novo corpore ex hydrogenio et carboneo composito," disseruit Fr. C. Himly, Göttingen, 1835. *Ann.*, **27,** 40 (1838).

a low-boiling fraction which he called "faradayin," and a high-boiling fraction which he called "caoutchene."

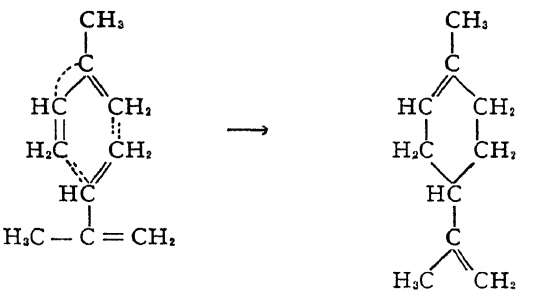
A hydrocarbon having a boiling point of 37° to 38° C., was later isolated from faradayin by Williams.[98] He termed this substance isoprene, but did not have the pure compound. Tilden[99] proposed the present structural formula for isoprene,

$$CH_2 = \overset{\displaystyle CH_3}{\overset{|}{C}} - CH = CH_2$$

The correctness of this formula was confirmed by Ipatiew and Wittorf.[100] W. Euler[101] established final proof for the formula by synthesizing isoprene from β-methylpyrrolidine. Ipatiew[102] also found trimethylethylene in the low-boiling faradayin fraction.

The discovery of isoprene in the distillation products of rubber was of the greatest importance in the determination of the constitution of rubber. It was soon found that isoprene, on prolonged standing, again formed rubber-like products. Isoprene and rubber are therefore genetically related. It was, of course, a long step from these first casual and non-reproducible observations to the actual preparation of synthetic rubber from isoprene (*see* p. 240 ff.).

Wallach[103] showed that caoutchene contained dipentene. The formation of dipentene and other terpenes from two molecules of isoprene was first explained by Wallach. Today, in the light of Thiele's theory of partial valences, we consider the formation of dipentene as resulting from the 1,4-addition of one molecule of isoprene to the 1,2-position of a second molecule of isoprene, according to the following scheme:



Dipentene has also been prepared synthetically by W. H. Perkin, Jr.[104] Bouchardat[105] reported that the dry distillation of 5 kilograms of rubber produced three fractions in the following quantities:

250 grams isoprene	= 5 per cent;	b.p. about	18-100° C.
2000 grams dipentene	= 40 per cent;	b.p. about	100-200° C.
600 grams heveene	= 12 per cent;	b.p. above	200° C.

Harries[106] deserves mention for further progress in identifying the decomposition products from the distillation of rubber at atmospheric pressure. The

[98] *J. Chem. Soc.*, **15**, 110 (1862).
[99] *J. Chem. Soc.*, **45**, 410T (1884); *Chem. News*, **46**, 129 (1882).
[100] *J. prakt. Chem.*, (2), **55**, 1, (1897).
[101] *Ber.*, **30**, 1989 (1897); *J. prakt. Chem.*, (2), **57**, 131 (1897).
[102] *J. prakt. Chem.*, (2), **55**, 2 (1897).
[103] *Ann.*, **227**, 292 (1885).
[104] *Proc. Chem. Soc.*, **20**, 86C, 1604 (1904); *J. Chem. Soc.*, **85**, 654 (1904).
[105] *Bull. soc. chim.*, (2), **24**, 108 (1875); see also *Ann.*, **27**, 30 (1838).
[106] Harries, "Untersuchungen . . . . . ," p. 10.

quantities of the fractions reported by Bouchardat could not be confirmed by Harries. He obtained only 3 per cent of pure isoprene (based on the weight of the rubber), boiling at 33° to 34° C. Harries further separated the dipentene fraction boiling at 150° to 200° C., by distillation at 15 to 16 mm. pressure, and obtained three fractions. While the first two fractions contained no dipentene, the third fraction consisted largely of dipentene.

Fraction I, after drying over sodium, boiled at 147° to 150° C., under a pressure of 761 mm., was colorless, and had an unpleasant odor. $d^{20.5} = 0.8286$, $n_D^{20.5} = 1.4902$.

Molecular refraction: Calcd. for $C_{10}H_{16}$: 44.92. Found: 45.24.
Elementary analysis: Calcd. for $C_{10}H_{16}$: C, 88.15; H, 11.85. Found: C, 86.15; H, 12.11.

Harries thought that this fraction contained a hydrocarbon of the open-chain type.

Fraction II, after drying over sodium, boiled at 168° to 169° C., at 761 mm. pressure, was colorless, possessed the odor of dipentene, but did not form dipentene tetrabromide or terpinene nitrosite; with bromine a characteristic deep violet color was obtained; $d^{20} = 0.8309$, $n_D^{20.5} = 1.45856$.

Molecular refraction: Calcd. for $C_{10}H_{16}$: 44.92. Found: 45.54.
Elementary analysis: Calcd. for $C_{10}H_{16}$: C, 88.15; H, 11.85. Found: C, 87.58; H, 12.00.

Harries suspected the existence of a new terpene in this hydrocarbon.

The fraction boiling above 200° C., the "heveene" of Bouchardat, was formed in the largest amount, and consisted of viscous oils, with boiling points up to 300° C. Harries could not obtain the characteristic nitrosite reaction for rubber from the highest boiling fraction.

Rubber shows an essentially different behavior when it is distilled in high vacuum. E. Fischer and Harries,[107] in a short communication, called attention to the fact that the dry distillation of rubber in high vacuum increased the proportion of high-boiling fraction, at the expense of the low-boiling fraction. According to Harries,[108] the distillation of rubber at 0.1 mm. pressure produced, in addition to a small amount of isoprene, principally a thick, oily mixture boiling between 220° to 260° C., from which no solid nitrosite could be obtained by treatment with nitrous acid. Unchanged rubber was therefore not present in the distillation products of rubber at low pressures.

The decomposition products of rubber in high vacuum were recently investigated by Staudinger and Fritschi.[109] According to these investigators, purified rubber began to swell when the temperature of the metal bath reached 220° to 250° C. Distillation then proceeded at a uniform rate if the temperature of the bath was maintained between 300° and 330° C. Towards the end of the distillation it was necessary to raise the temperature to 350° C. The yield of the distillate was 63.5 per cent, part of which had condensed in a receiver cooled to —80° C. The remaining 36.5 per cent was obtained as a resinous residue in the distillation flask. If the distillation was conducted rapidly, the amount of distillate could be increased to 95 per cent, according to Staudinger.

The distillate was then fractionated in a Ladenburg flask at 0.03 mm. pressure and separated into eleven fractions. A receiver cooled to —80° C., served to condense the more volatile constituents. Table 2 gives the percentage yields which Staudinger and Fritschi obtained by the fractionation of the rubber decomposition products.

[107] *Ber.*, **35**, 2142 (1902). [108] *Ann.*, **383**, 204 (1911). [109] *Helv. Chim. Acta*, **5**, 796 (1922).

TABLE 2.—*Fractional Distillation According to Staudinger and Fritschi.*

Fraction	Temperature of oil bath ° C.	Boiling point ° C.	Yield Grams	Yield Per cent
1	Room temperature	Condensed at—80°	10.1	5.6
2	80 - 88	45 - 46	21.0	11.6
3	90 - 110	46 - 60	7.8	4.4
4	114 - 124	60 - 85	9.5	5.3
5	124 - 142	85 - 100	14.9	8.3
6	144 - 170	100 - 150	14.6	8.1
7	220 - 240	150 - 170	29.8	16.5
8	240 - 250	170 - 190	14.0	7.7
9	270 - 300	190 - 220	26.5	14.7
10	310 - 345	220 - 255	14.5	8.0
11		Resinous residue about	15.0	8.3

The following substances were identified in the eleven fractions:

Three per cent of crude isoprene (based on the weight of the rubber) with a boiling range of 30° to 50° C., was obtained in the receiver cooled to -80° C.

The remainder of fraction 1 and fraction 2 contained 30 grams of dipentene, which was identified by preparing the bromide and the hydrochloride. An aliphatic diterpene and a cyclic terpene, isomeric with dipentene, which were obtained by Harries[110] in the distillation at atmospheric pressure, could not be obtained by Staudinger.

Fractions 3, 4 and 5 consisted of a hydrocarbon $C_{15}H_{24}$ containing two double bonds. A diterpene with three double bonds was present in fractions 6 and 7.

From the highest boiling portion of fraction 7 and from fraction 8 a hydrocarbon $C_{25}H_{40}$ was isolated.

Staudinger assumed that fractions 9 and 10 contained hydrocarbons of the formula $C_{30}H_{48}$ and $C_{35}H_{56}$.

The elementary analyses of the above-mentioned substances always gave values for carbon which were about 1 per cent too low. Staudinger attributed this difference to an auto-oxidation of the hydrocarbon. Table 3 gives the physical properties of the purest fractions.

TABLE 3.—*Physical Constants of Fractions According to Staudinger and Fritschi.*

Composition	Mol. wt. Calcd.	Mol. wt. Found	Boiling Point ° C.	d_4^{20}	n_D^{20}	M_D Calcd.	M_D Found
$C_{10}H_{16}$ 2 double bonds, 1 ring	136	142,000	58 (11 mm.)	0.8390	1.4724	45.24 Fraction 2.	45.24
$C_{15}H_{24}$ 3 double bonds, 2 rings	204	200,000	88-91 (0.05 mm.)	0.8895	1.4980	66.13 Fraction 2.	67.23
$C_{20}H_{32}$ 3 double bonds, 2 rings	272	268,267	118-122 (0.02 mm.)	0.9046	1.5065	88.76 Fraction 3.	89.41
$C_{25}H_{40}$ 4 double bonds, 2 rings	340	303,316	142-148 (0.04 mm.)	0.9161	1.5119	111.37 Fraction 4.	111.2

The number of double bonds was determined by titration with a 0.5 *N* solution of bromine in chloroform.

The dry distillation of rubber has yielded, in addition to isoprene, a number of its polymers which contain the same percentages of carbon and hydrogen. The study of this reaction has therefore definitely shown that the rubber hydrocarbon is an isoprene polymer of high molecular weight having the formula $(C_5H_8)_x$. The chain composed of isoprene units is cracked by

[110] Harries, "Untersuchungen . . . . . ," p. 10. Cf. Ber., **35**, 3266 (1902).

pyrogenetic distillation in such a manner that only isoprene or its polymers are produced. The weak linkages of this chain at the ends of the group

$$\longleftarrow CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\longrightarrow$$

recall the great reactivity of the allyl halides. Staudinger was led to the hypothesis that the long chain rubber molecule built up of isoprene units can dissociate in solution at room temperature or at slightly elevated temperatures, and that dissociation occurs between groups of the diallyl type, according to the following scheme.

$$CH_3 \qquad\qquad CH_3$$
$$-CH_2-\overset{|}{C}=CH-CH_2-$$

Other polyprene radicals are attached at the arrows and the point of dissociation is indicated by dots. The dissociation is similar to that of hexaphenylethane, and results in radicals containing trivalent carbon. It should be possible to detect these radicals by a sharp absorption band in the ultraviolet spectral region, which, according to Scheibe and Pummerer,[111] is not observed. These radicals would, furthermore, be expected to react at once with iodine, but no such reaction could be observed.

Midgley and Henne* [*J. Am. Chem. Soc.*, **51**, 1215 (1929)] have reinvestigated and extended the earlier work on the destructive distillation of rubber, for the purpose of determining the constitution of rubber. Rubber was destructively distilled at atmospheric pressure. The temperature was always rapidly raised to 700° C. Rubber was also distilled in the presence of metals such as magnesium, zinc, copper, iron, and aluminum. Ten per cent of the distillate consisted of isoprene and 20 per cent consisted of dipentene. The yields of the other compounds in the distillate were low. The compounds in the distillate were olefinic, dienic, aromatic and hydro-aromatic in character. The compounds identified were: 3-methyl-1-butene, 2-methyl-1-butene, isoprene, 2-methyl-2-butene, 2-methyl-2-pentene, benzene, Δ^1-tetrahydrotoluene, toluene, *m*-xylene, *p*-tetrahydroethyltoluene, *p*-ethyltoluene and dipentene. Neither myrcene nor a terpene boiling at 168° to 169° C. was found in the distillate. Midgley and Henne assume that the long chain molecule of rubber, proposed by Staudinger, breaks at single valences, that the points of breakage are represented by partial valences, and that the double bonds are resolved into partial valence forms. The formation of the resulting stable compounds can then be explained by the following postulates: (1) adjacent partial valences may join to form double bonds; (2) single partial valences six carbon atoms apart may join to form rings; (3) any pair of partial valences, preferably those not adjacent to others, may accept hydrogen; (4) partially hydrogenated aromatic compounds liberate hydrogen to yield the corresponding aromatic compounds; (5) partial valences not joining nor accepting hydrogen may migrate. Nearly all of the compounds predicted could be isolated from the distillate.

T. Midgely, A. L. Henne and A. F. Shepard [*J. Am. Chem. Soc.*, **54**, 2953 (1932)] have also identified the following compounds in the products obtained from ebonite by destructive distillation: 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-dimethylthiophene and *m*-xylene.

The destructive distillation of rubber (pale crepe) in the presence of anhydrous aluminum chloride has also been reported [Zelinsky and Koslow, *Ann.*, **497**, 160 (1932); *Rubber Chem. Tech.*, **6**, 64 (1933)]. The decomposition of the rubber with $AlCl_3$ takes place at a lower temperature than without $AlCl_3$. Two hundred grams of pale crepe rubber when distilled with 10 per cent by weight of $AlCl_3$ yield 69 per cent of liquid products and 14 liters of gaseous products. No isoprene was found in the products of distillation. The liquid distillate contains saturated light oils of the benzine

[111] *Ber.*, **60**, 2163 (1927).

* Translator's Note.

series, as well as unsaturated heavy oils of the same series. Destructive distillation in the presence of larger amounts of $AlCl_3$ (20 per cent by weight of the rubber) yields a distillate which contains benzine hydrocarbons, which are completely saturated. The hydrocarbons resulting from the distillation are largely cyclo-alkanes. The mechanism of the thermal decomposition of rubber in the presence of anhydrous aluminum chloride is therefore different from the thermal decomposition of rubber alone.

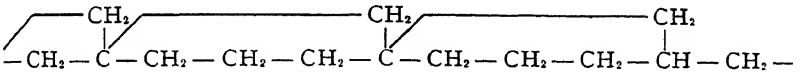
The largest yield of isoprene obtained from rubber by destructive distillation was obtained by H. L. Bassett and H. G. Williams (*J. Chem. Soc.*, **1932**, 2324). Pieces of solid rubber were dropped on a hot surface and the products of pyrolysis were quickly removed and cooled. In this way a yield of 16.7 per cent of isoprene was obtained. Treatment of the higher-boiling fractions according to a modification of Harries' "isoprene lamp" method gave a total over-all yield of 23 per cent isoprene.

CYCLIZATION BY HEATING

Without Acid

Staudinger and Geiger [112] carefully studied the effect of heat on rubber under circumstances such that complete cracking was avoided, and found that under these conditions the number of double bonds diminished. When heated in an indifferent medium, a good grade of crude rubber becomes soft at 200° C. without undergoing any profound change. The number of double bonds which can be determined remains approximately the same. Solutions of the heated rubber have a much lower viscosity than solutions of the original rubber. Lowering of the viscosity may be caused either by disaggregation or by degradation of the rubber.

Above 250° C., a fundamental change occurs in the rubber, resulting in the removal of the double bonds and the formation of rings. There is formed a polycyclo-rubber which the above authors formulate in the following manner:



This change is best brought about by heating rubber for several hours in ether solution at 250° C. The cyclic product thus obtained still contains one double bond for every five isoprene units, four of the isoprene units having combined to form a ring. The appearance of the rubber has also completely changed. Polycyclo-rubber is a light yellow powder which no longer possesses the properties of rubber. Solutions of polycyclo-rubber are only slightly viscous. The cryoscopic molecular weight determination in benzene no longer gives indeterminable values, but values corresponding to a molecule composed of 30 isoprene groups. Cyclization of the rubber molecule has brought about an increase in density, which usually accompanies ring formation. Rubber has a density of 0.920 (d_4^{16}), polycyclo-rubber a density of 0.992 (d_4^{16}) whether it is obtained by heating rubber or from the hydrobromide of rubber.

The double bond which remains after cyclization can be hydrogenated and reacts normally toward bromine, sulfur chloride, and ozone. The hydrocyclorubber produced by hydrogenation has a molecular weight (measured in benzene) of 2050, which agrees with the value for cyclorubber and with the value obtained by Pummerer for the molecular weight of rubber when determined in camphor.

[112] *Helv. Chim. Acta*, **9**, 549 (1926).

It is very probable that polymerization accompanies cyclization when rubber is heated. It is also very probable that the polymerization of rubber with tin tetrachloride, according to the method of Bruson,[113] is accompanied by cyclization of the rubber molecule.

In the pyrogenetic decomposition of polycyclo-rubber there is obtained a complex mixture of cyclic compounds, from which dipentene has not been isolated. Rubber, on the other hand, yields considerable quantities (up to 12 per cent) of pure dipentene when heated to about 300° C. without a solvent in an atmosphere of carbon dioxide at ordinary pressure. Thirty per cent of the weight of the rubber distils over, of which 40 per cent is dipentene and the remainder is composed of sesqui-terpenes and higher terpenes. The residue, when further heated in high vacuum, yields 20 per cent more of higher boiling hydrocarbons. Forty per cent by weight of the rubber used remains in the flask in the form of a brittle resin, which is nothing but cyclo-rubber, and which can be purified by extracting with ether and reprecipitating with alcohol.

The results of these investigations, especially the formation of large quantities of dipentene and the formation of cyclo-rubber at the beginning of the pyrogenetic decomposition, may later be of great importance in determining the constitution of rubber.

With Hydrochloric Acid and Zinc Dust

Harries and Evers [114] believed that they had succeeded in bringing about a partial hydrogenation of rubber in the form of its hydrochloride. These authors dissolved rubber in ethylene chloride, saturated the resulting solution with hydrochloric acid, and then reduced the rubber hydrochloride with zinc dust. They obtained the *alpha*-hydrorubber as a white solid product which was still unsaturated after purification.

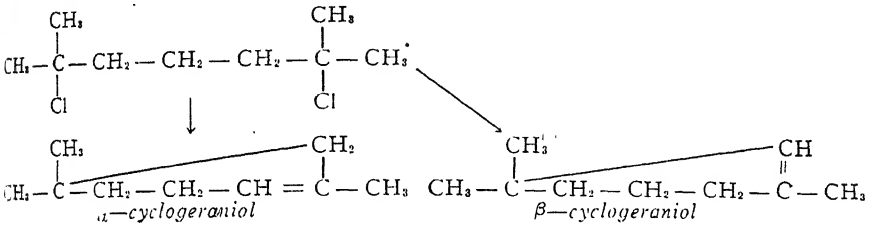
According to recent investigations by H. Staudinger and W. Widmer,[115] hydrogenation does not occur in the reduction of rubber hydrochloride with zinc dust, but rather an inner condensation (cyclization). The reduction product is a fluffy white powder, which still contains one-half the double bonds of the rubber (monocyclo-rubber).[116] Upon repeating the treatment with hydrogen chloride and zinc dust, there is formed a polycyclo-rubber which contains only one double bond for each 3 to 4 isoprene groups.[117] The dry distillation of the product in a manner similar to the dry distillation of rubber gave a mixture of hydrocarbons boiling at various temperatures. In contrast to the results obtained in the distillation of natural rubber, Staudinger could not isolate dipentene from the distillate. In the process of cyclization, there are formed cyclo-rubbers which differ widely in mean molecular weight, depending upon the boiling point of the solvent in which the rubber is heated with hydrochloric acid or hydrobromic acid (tetralin 2,000, toluene 4,000, xylene 10,000). The cyclo-rubbers are only partly soluble in ether, but are very readily soluble in the other usual rubber solvents. They can be distinguished from rubber by a comparison of their molecular refractions.

[113] *Ind. Eng. Chem.*, **19**, 1033 (1927).
[114] *Mitt. Forschungsinst. Siemens-Konzern*, **1**, 87-95 (1922); *C. A. Abstracts*, **16**, 3232 (1922).
[115] *Z. angew. Chem.*, **38**, 227 (1925); *Helv. Chim. Acta*, **9**, 529 (1926); also *Ann.*, **468**, 47 (1929), where the cyclization of gutta-percha is described.
[116] The monocyclo-rubber might better be termed hemicyclo-rubber.
[117] *Cf.* above, "Cyclization by Heating."

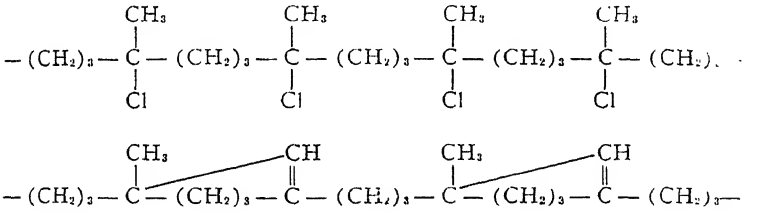
The catalytic hydrogenation of the so-called mono- as well as the polycyclo-rubber leads to the same hydropolycyclo-rubber of empirical formula $(C_{20}H_{34})_x$, in which only every fourth isoprene group has added one molecule of hydrogen.[118]

Still more noteworthy is the behavior of mono- and polycyclo-rubber toward oxidizing agents such as ozone or permanganate. The reaction product formed by these reagents has the empirical formula $(C_5H_8O)_x$, and is an amorphous, insoluble material. Such a substance is occasionally obtained from rubber by the action of the above oxidizing agents.

Staudinger also treated 2,6-dimethyl-2,6-dichlorheptene with zinc dust and hydrochloric acid, and considered that the cyclogeraniol (C_9H_{16}) formed was produced by a reaction analogous to the previously discussed reaction (cyclization) of the rubber hydrochlorides. The reaction can be represented in the following manner:



A mixture of two isomers is formed. In a similar manner, the formation of monocyclo-rubber from rubber hydrochloride is represented as follows by Staudinger and Widmer:



The position of the double bond in the case of the beta-cyclogeraniol is arbitrarily chosen. Splitting off of hydrogen chloride certainly takes place in the most diverse ways. The synthesis of higher hydrocarbons from lower members is also possible through cyclization, involving different molecules, and very likely proceeds in this manner. The above authors, for example, obtained a diterpene by the action of zinc dust on dipentene-dihydrohalide.

H. L. Fisher* [*Ind. Eng. Chem.*, **19**, 1325 (1927), U. S. Pat., 1,605,180 (1926); Can. Pat., 256,567 (1925); *Ind. Eng. Chem.*, **19**, 1325 (1927); see also Kirchhof, *Kautschuk*; **4**, 142-148 (1928); **5**, 47, 65 (1929)] by treating rubber directly with sulfuric acid on the mill, obtained thermoplastic products which have found commercial application. He also milled rubber with chlorosulfonic acid ($HOSO_2Cl$), organic sulfonic acids, and

[118] The direct cyclization of rubber in the abnormal catalytic hydrogenation by means of platinum and hydrogen is discussed on p. 229. This type of cyclization was the first to be described in the literature. According to Staudinger and E. Geiger (dissertation, Zürich, **1926**), cyclization, as well as hydrogenation, can readily be followed by measuring the molecular refraction.

* Translator's Note.

sulfonyl chlorides, e.g. p-toluene sulfonyl chloride, β-naphthalene sulfonyl chloride and other sulfonic acids and sulfonyl chlorides. When the milled rubber containing the above organic acids or acid chlorides, is sheeted out and heated at 125° to 135° C., the rubber is converted into tough thermoplastic products resembling gutta-percha and balata. If heated similarly in bulk the products formed are hard and thermoplastic, like shellac. These products which have been given the general name "thermoprene" are hydrocarbons of high molecular weight with the same composition as rubber $(C_5H_8)_x$.

Bruson, Sebrell and Calvert [*Ind. Eng Chem.*, **19**, 1033 (1927)] also treated rubber in solution with stannic chloride, ferric chloride, titanium chloride, and antimony pentachloride. Addition products are formed which when treated with alcohol also yield products similar to those obtained by Fisher with organic sulfonic acids. Evers (*Kautschuk*, **1**, 8, Nov. 1925) has also treated a solution of rubber in chlorbenzene with aluminum chloride. When ferric chloride or other amphoteric metal halides are mixed into rubber on the mill, and the resulting mixture is heated to 175° C., similar products are obtained [Jones and Winkelmann, Chem. Abstracts, **21**, 1031 (1927); Can. Pat., 267,116 (1926)].

All of the above-described products are less unsaturated than the original rubber hydrocarbon. Cyclization of the rubber hydrocarbon has probably taken place, and the resulting products are classified under the term "polycyclo-rubber." For an excellent summary of the work in this field, *see* Fisher, "The Chemistry of Rubber," *Rubber Chem. Tech.*, **7**, 115 (1930).

A reaction product of rubber with benzyl chloride in the presence of anhydrous $AlCl_3$ has been described by Kirchhof. The reaction is carried out by pouring anhydrous aluminum chloride suspended in CCl_4 quickly into a cooled rubber—carbon tetrachloride-benzyl chloride solution. Hydrochloric acid is evolved and a grayish-white spongy mass is formed, which remains as a white amorphous product. The product swells very little in organic solvents and is almost insoluble in the common organic solvents. At 100° C. the product is slightly thermoplastic. In contrast to the cyclorubbers which are still 20 per cent to 30 per cent unsaturated, the new product is quite inert toward halogens and oxygen. The new product is known as "benzylidene rubber." Its constitution has not been established, but the empirical formula corresponds to a compound of the composition $(C_{36}H_{38})_x$. A substance of this composition would correspond to the reaction of three molecules of benzyl chloride with one C_5H_8 group, *Kautschuk*, **7**, 128 (1931); *Rubber Chem. Tech.*, **5**, 110 (1932).

The Effect of Heat on Rubber in Solution

H. Staudinger and H. F. Bondy [119] found that solutions of gutta-percha in benzene or in toluene could be heated for weeks in an atmosphere of carbon dioxide without altering the original viscosity of the solutions after they were again cooled. When gutta-percha was heated in xylene, however, a decrease in the relative viscosity of the solutions occurred.[120] When solutions of crude rubber or alkali-purified total rubber, in benzene or in toluene, were heated for one day, a decrease in the viscosity of the solutions had occurred. The original viscosity after cooling continued to decrease from day to day until, after heating for ten to fourteen days, the change was considered complete. Heating in xylene, because of its higher boiling point, produced a more rapid decrease in the viscosity of the solution and a lower final value. It is noteworthy that the final value for the viscosity was not appreciably changed by replacing xylene with the higher boiling tetralin (206° C.).

Staudinger made similar observations with the highly viscous polystyrenes having the highest molecular weight. He makes the very plausible assumption that in the polymerization of an unsaturated hydrocarbon (styrene, isoprene) the mean molecular size of the high molecular weight polymers depends upon the temperature of polymerization. A system of high molecular weight polymers which would be unstable at a certain temperature,

[119] *Ann.*, **468**, 1 (1929).

[120] The viscosity of the solution before heating is denoted by η_1, and the viscosity after heating by η_2. The decrease in viscosity is represented by $\frac{\eta_1}{\eta_2}$ and after heating in benzene for 10 days was equal to 1.98.

would be stable at lower temperatures. If such a system which had actually attained polymerization equilibrium [121] at certain temperatures were heated, smaller fragments of the original molecules would be formed. Thus degradation of the gutta-percha molecule first takes place in boiling xylene at a temperature of 142° C. With rubber the change takes place in boiling benzene and in toluene. For this reason it is estimated that the molecular weight of rubber is greater than that of gutta-percha. This view is confirmed by the relative viscosities of these two substances, which, when compared with the viscosities of the polystyrene fractions, point to very large molecules (the so-called macromolecules) in both cases. It is estimated that the molecular weight of rubber is greater than 100,000; and that the molecular weight of gutta-percha is greater than 50,000. In the light of this hypothesis, the high molecular weight of rubber is given as an explanation for its low thermal stability.

Up to a temperature of 150° C., no diminution in the number of double bonds is observed when solutions of rubber are titrated with iodine chloride. Staudinger assumes that at higher temperatures the long chain rubber molecules crack into shorter ones possessing the same degree of saturation, without undergoing cyclization. Only at a temperature of 142° C. (in boiling xylene) are molecules first formed of such a size that a cryoscopic determination of the molecular weight in benzene is possible. The rubber recovered from the solvent gives average molecular weight values of 4,200, while recovered gutta-percha gives values of 2,800. At a higher temperature (206° C.) the values are respectively 3,400 and 6,400. At the higher temperature, partial cyclization takes place and in the case of gutta-percha the cyclic compounds are apparently further polymerized to cyclic products of higher molecular weight. The products recovered from toluene and xylene are viscous and tacky in the case of rubber, and solid in the case of gutta-percha. The properties of the original substances are thus retained to some degree.

The results of molecular weight and viscosity determinations, as well as of titration experiments, are frequently unreliable, because of auto-oxidation of the sample during the prolonged boiling in an atmosphere of carbon dioxide. This is especially true in the important experiments carried out in xylene in which the rubber recovered from the solvent in high vacuum at 80° C. can not be brought to constant weight. On analysis, the hydrocarbons resulting from the degradation of the rubber show an oxygen content of 1.5 to 2.0 per cent, for which reason deficiencies up to 6 per cent in the determination of the number of double bonds are disregarded. Oxygen-containing decomposition products or their transformation products, which were not removed by drying in high vacuum, are also included in the measurements.

Staudinger and Bondy consider these experiments on the thermal degradation of rubber, which result in the cracking of macromolecules of indeterminable size into smaller molecules of varying size, as proof that rubber cannot be composed of a small unit molecule consisting of eight to sixteen isoprene groups. On the basis of this assumption, they are of the opinion that their observations are to be explained by polymerization reactions. Such reactions are entirely possible, since polymerization reactions have been shown to take place when sol-rubber is heated (*see* p. 184). At that point the reactions were interpreted as aggregation, which also has the same tendency toward

[121] This is more likely to be the case with a polystyrene which requires many years for its formation, than with rubber in latex, which is collected daily.

increasing the viscosity as does the formation of molecules of increasing size. Reactions between two or more molecules to produce high molecular weight polymers are less likely to occur in solution than in the undiluted condition, but they are nevertheless possible, as are also decomposition and rearrangement. Staudinger and Bondy assume that such reactions take place on heating gutta-percha from 142° C. to 206° C. If such an open-chain molecule of finite size is cracked only into smaller open-chain molecules the number of double bonds must necessarily increase. If the number of double bonds does not increase in spite of the decreasing molecular size, it could be concluded that cyclization had taken place. It should be mentioned that all rubber solutions studied by Staudinger and Bondy, because of the crepe and total rubber used, should show an abnormal viscosity behavior, namely structural viscosity (displacement elasticity).

According to Kruyt,[122] it is to be suspected that all solutions of lyophilic colloids are capable of gelatinizing. With gelatine and agar, swelling temperatures are known above which the viscosity of the solutions becomes normal. In this case, however, the abnormalities are reversible, and Staudinger and Bondy emphasize especially the irreversible nature of the degradation reactions of rubber which they investigated. It must also be remembered that, at least with rubber, the solutions still contain the swollen "hull substance" of the rubber globules, provided previous solution has not taken place. These "botanical" particles are, of course, irreversibly destroyed. Even though they are not destroyed, the re-formation of the original aggregates may possibly require long standing of the dry products recovered from solution.

The conclusiveness of this work of Staudinger and Bondy for the existence of macromolecules of rubber and gutta-percha is therefore still doubtful. A purely colloidal chemical explanation seems probable.[123]

The viscosities of solutions of rubber are very largely dependent on nitrogen-containing and other impurities. This is shown by the great difference in viscosity between solutions of raw rubber and of pure rubber. Solutions of pure rubber (varying with the concentration) possess only one-fourth to one-ninth the viscosity of solutions of raw rubber of the same concentration. Even purified rubber is not completely nitrogen-free (*see* p. 173).

Halogen Derivatives of the Rubber Hydrocarbon

The colloidal nature of the rubber hydrocarbon makes difficult its chemical investigation. For this reason, early attempts were made to prepare definite homogeneous derivatives, by the aid of which proof of its constitution and molecular size could have been obtained. Rubber, since it is an unsaturated hydrocarbon, reacts principally at the carbon double bonds. These reactions prove that one double bond is present for each C_5H_8 group. The addition products with the halogens and halogen acids will be first discussed.

[122] *Kolloid-Zeitschr., Beihefte*, **28**, 1, 1928.
[123] See also K. H. Meyer, *Naturwissenschaften*, **17**, 255 (1929), and Pummerer, *Kautschuk*, **5**, 129 (1929).

HALOGEN ADDITION PRODUCTS

Addition of Chlorine

Gladstone and Hibbert [124] treated a one per cent chloroform solution of rubber with chlorine. On evaporating the solution, they obtained a light yellow substance of the composition $C_{10}H_{14}Cl_8$.

The reaction was repeated by Hinrichsen, Quensell, and Kindscher,[125] who cooled the solution of rubber in an ice bath. After reprecipitating the reaction product several times, they isolated a white amorphous substance the composition of which indicated the formula, $C_{10}H_{14}Cl_6$.

These substances are probably not homogeneous. A pure addition product of the formula, $C_{10}H_{16}Cl_4$, analogous to the tetrabromide to be described, could not be isolated. The addition of chlorine to the rubber hydrocarbon is always accompanied by the formation of hydrogen chloride, which is produced by substitution or more probably by splitting off hydrogen chloride from the dichloride.[124a]

Addition of Bromine

The bromine addition product of rubber is of far greater importance, since a quantitative method for the determination of the rubber hydrocarbon is based on this addition reaction.

The earliest work on rubber bromide was done by Gladstone and Hibbert.[126] These investigators obtained the bromide by the action of bromine on rubber dissolved in chloroform, and were the first to obtain the so-called rubber tetrabromide $C_{10}H_{16}Br_4$. They obtained a by-product, $C_{10}H_{15}Br_5$, which they supposed might well be formed by the elimination of hydrogen bromide from the normal addition product, $C_{10}H_{16}Br_6$, (assuming three double bonds in the complex, $C_{10}H_{16}$). The tetrabromide has a tendency to split off hydrogen bromide on evaporating its chloroform solution. Weber,[127] in order to avoid this, did not evaporate the solution, but precipitated the bromide by the addition of alcohol. Weber described the tetrabromide as a white substance insoluble in the usual rubber solvents. The elimination of hydrogen bromide can be prevented by preparing the compound in the cold. On heating the bromide to 50°-60° C., a lively evolution of hydrogen bromide takes place and the white compound becomes discolored. The complete removal of bromine can not be accomplished even at a temperature of 150° C. The tetrabromide, as in the case of all halogen addition products, is a compound of high molecular weight, the magnitude of which cannot be determined by the usual methods, since determinations at higher temperatures are excluded. The analytical figures agree well with the formula, $C_{10}H_{16}Br_4$. It dissolves in aniline and pyridine with partial decomposition. The composition of the tetrabromide is best expressed as a dibromide of the formula $(C_5H_8Br_2)_x$.

The quantitative determination of rubber as the bromide, referred to above, is best carried out according to the method of Budde and Hübener,[128] as follows:

A 0.15 to 0.2 gram sample of the rubber is allowed to swell in carbon tetrachloride, and is then treated with 50 grams of a bromine solution consisting of 5 cc. of

[124] *J. Chem. Soc.*, **53**, 682T (1888).
[124a] Kirchhof, *Farben-Ztg.*, **37**, 552 (1932).
[125] *Ber.*, **46**, 1284 (1913).
[126] *J. Chem. Soc.*, **53**, 682T (1888).
[127] *Ber.*, **33**, 786 (1900).
[128] *Gummi-Ztg.*, **23**, 6 (1909).

bromine and 1 gram of iodine carrier dissolved in a liter of carbon tetrachloride. After standing for 6 hours, during which the mixture is frequently shaken, the tetrabromide is precipitated by the addition of a quantity of alcohol equal to one-half the volume of the solution. The quantity of rubber hydrocarbon can be calculated directly from the weight of the tetrabromide, or from the weight of silver bromide obtained by the determination of bromine in the precipitate. Excessive bromination can be avoided by cooling in an ice bath, according to the procedure of Hinrichsen and Kindscher (*see* p. 391).

Harries [129] observed that the evolution of hydrogen bromide always accompanied the formation of the tetrabromide. He states that the tendency of the tetrabromide to liberate hydrogen bromide increases with the purity of the starting material. This evolution proceeds more readily on warming, but the complete removal of bromine with alcoholic potash is accomplished only with difficulty.[130]

Weber [131] treated the tetrabromide with sodium phenolate, and isolated three distinct phenol derivatives of rubber. They are soluble in alkali, acetone, and ether, and insoluble in chloroform, carbon disulfide and hydrocarbons. We are indebted to Staudinger and Geiger [132] for a thorough investigation of these derivatives. From the alkali solubility of these substances, it is to be expected that they contain phenolic hydroxyl groups and that the phenolic groups are linked to the carbon atom of the rubber molecule through the elimination of hydrogen halide. They are hydroxyl derivatives of rubber diphenyl. Various phenol derivatives can be prepared from the dibromide $(C_5H_8Br_2)_x$, with the aid of ferric chloride, at temperatures of 90° to 120° C. The reaction proceeds with vigorous evolution of hydrogen bromide. It is possible to replace the two bromine atoms by phenol, cresol, resorcinol, or pyrogallol, which are attached to the rubber hydrocarbon at the ring.[133] These products can be coupled with diazo compounds in the usual manner. Furthermore, the hydroxyl groups of the phenol derivatives can be benzoylated according to the Schotten-Baumann reaction. The phenol ethers, such as anisole and phenetole, react more slowly with the dibromide. The dibromide of gutta-percha also reacts with the various phenols, to give derivatives analogous to the rubber derivatives with phenol.

Addition of Iodine

Weber [134] obtained an iodine derivative by treating a three per cent carbon disulfide solution of rubber with an excess of iodine. The reaction mixture solidified to a jelly after twelve hours. The filtered reaction product was washed with alcohol and was an egg-yellow powder which was soluble in warm aniline and in piperidine. When preserved, it decomposed with separation of iodine (this took place rapidly in sunlight) and became brown. An elementary analysis indicated a substance of the composition, $C_{20}H_{32}I_6$.

The action of iodine on rubber was further investigated by Hinrichsen and Kempf.[135] They allowed a one per cent solution of iodine in chloroform to react with a one per cent rubber solution, and showed that the mixture was rapidly decolorized in direct sunlight. They isolated the iodine derivative by pouring the mixture into benzene, and obtained a white powder which contained not only iodine, but also oxygen. Hinrichsen and Kempf doubt the existence of the iodine derivative prepared by Weber and refrain from assigning a formula to their compound.

[129] Harries, "Untersuchungen . . . . . ," p. 12.
[130] Kirchhof, *Kolloid-Z.*, **15**, 126 (1914).
[131] *Ber.*, **33**, 786 (1900).
[132] *Helv. Chim. Acta*, **10**, 530, 539 (1927).
[133] See also, Fisher, Gray and McColm, *J. Am. Chem. Soc.*, **48**, 1309 (1926).
[134] *Ber.*, **33**, 789 (1900).
[135] *Ber.*, **46**, 1288 (1913).

The determination of the iodine number of rubber according to a slightly modified Wijs method, by means of iodine chloride in chloroform solution, was recommended by H. L. Fisher and A. E. Gray.[136] They found that crude rubber reacts with 95 to 96 per cent of the iodine required by the theory which postulates one double bond, and therefore the addition of one molecule of iodine, for each C_5H_8 group. Bruson [137] criticized this method adversely. Pummerer and Mann,[138] by observing certain precautions, found that the method was applicable when solutions of rubber varying in concentrations from 0.2 to 0.8 per cent were allowed to stand with approximately 0.2 *N* iodine chloride solution. It is immaterial whether the reaction is conducted at 0° C. or at room temperature, or whether the reaction mixture is allowed to stand six hours or ninety hours. The procedure for the determination (three parallel determinations) is conducted in the following manner:

At the end of the reaction, which requires six hours, 2 to 3 grams of potassium iodide are added to the chloroform solution, which is then shaken for several minutes. The bulk of the quantity of 0.1 *N* sodium thiosulfate necessary to combine with the excess iodine chloride (a 25 to 50 per cent excess is used) is added, and the titration is finished by the dropwise addition of the thiosulfate, using starch in the water layer as indicator. After the iodine has all been consumed, the free halogen acid is determined by means of 0.1 *N* sodium bicarbonate solution or normal sodium hydroxide solution. The acid content in the case of sol-rubber is about six per cent of the halogen consumed. In the dry reaction, no hydrogen halide is formed, if sol-rubber prepared from alkali-purified latex is used. With gel-rubber a considerable quantity of hydrogen halide is formed in the reaction. If it is assumed that this was formed by substitution, the high value for the unsaturation of gel-rubber is reduced to 98 to 100 per cent.[139] If water is added, sufficient additional quantities of the halogen acid are formed from the gel addition product, to make the total quantity of acid equal to 8 to 10 per cent of the halogen consumed. The iodine number, together with the oxygen number (given in parentheses) obtained according to Prileshajew's method (*see* Pummerer and Burkard, p. 209) is given in the following summary:

Sol from latex or Revertex: 100.3 (93.8).
Gel from latex: 108.6 (99.8); from Revertex: 110.2 (98.4).
Sol from smoked sheet: 98.3 (91.3); from crepe: 97.6 (91.2).
Gel from smoked sheet: 102.5 (94.5); from crepe: 110.3 (98.2).

The total rubber from crepe, latex, and Revertex give iodine values of 100.4, 101.5, 101.9 respectively.*

Addition of Hydrogen Halides

The addition products of the halogen acids with rubber show, as did the addition products of the halogens with rubber, that in the reaction one double bond has disappeared for each C_5H_8 group of the molecule. With the exception of the hydrofluoride, the halogen acid derivatives corresponding to the formula $(C_5H_8.HX)_x$ have all been prepared and characterized. These substances are not completely homogeneous, even when prepared from purified rubbers of the same analytical composition.

[136] *Ind. Eng. Chem.*, **18**, 414 (1926); see also, A. R. Kemp, *Ind. Eng. Chem.*, **19**, 531 (1927); A. R. Kemp and G. S. Mueller, *Ind. Eng. Chem., Anal. Ed.*, **6**, 52 (1934); R. Pummerer and H. Stärk, *Ber.*, **67**, 292 (1934).

[137] Bruson, *Ind. Eng. Chem.*, **19**, 1036 (1927).

[138] *Ber.*, **62**, 2636 (1929).

[139] It is questionable whether this is permissible, since the halogen acid could also result from cyclization, in which case it should not be subtracted.

* Translator's Note. Pummerer and Stärk [*Ber.*, **64**, 825-30 (1931); *Rubber Chem. Tech.*, **4**, 398-403 (1931)] have found that the above values for sol- and gel-rubber hold when a chloroform solution of rubber is titrated with a solution of iodine chloride in carbon tetrachloride. The excess of iodine-chloride used amounted to 20 per cent.

These authors also found that rubber reacts with dithiocyanogen, and that the addition of this reagent to the rubber corresponds to one molecule of dithiocyanogen per C_5H_8 group.

Hydrochloride

Weber [140] prepared the hydrochloride by passing moist hydrogen chloride into a chloroform solution of rubber. The hydrogen chloride is at first energetically absorbed. The end of the reaction is recognized by a large decrease in the original viscosity of the solution and by the darkening in color of the solution. If the reaction mixture is poured into alcohol, the hydrochloride separates as a white, stringy mass, which sometimes decomposes spontaneously into a white powder. Weber emphasizes the fact that the products obtained with dry hydrogen chloride are not of constant composition. When moist hydrochloric acid is used, the composition of the products is also variable. The values obtained from an elementary analysis are only in fair agreement with the calculated values for the formula C_5H_9Cl, the chlorine value always being from 0.5 to 3.0 per cent too low. No measurable depression is observed in the molecular weight determination, since the product is of high molecular weight. Solutions of the hydrochloride are much less viscous than those of rubber, because of the absence of double bonds in the molecule.[141] The hydrochloride is soluble in chloroform and benzene without decomposition. In pyridine and in piperidine, it decomposes with elimination of hydrogen chloride. For the preparation of the hydrochloride, Hinrichsen and Kindscher used purified rubber which had been reprecipitated with alcohol, and cooled the solutions of the rubber in an ice bath. They obtained a product which contained 2 per cent less chlorine than the amount required by the formula C_5H_9Cl. All hydrochlorides prepared thus far show variable values for the chlorine content.

Evolution of hydrogen chloride from the rubber hydrochloride begins when it is warmed to 40° C. According to Weber, the evolution of hydrogen chloride apparently ceases when the original chlorine content has been reduced from 33.9 per cent to 18 per cent. The remaining chlorine is assumed to be more firmly bound, and since no further elimination of hydrogen chloride occurs on heating this product to 130° C., Weber concludes that a substance of the formula $C_{10}H_{16}.HCl$ has been formed. The calculated chlorine content of a substance having the formula $C_{10}H_{16}.HCl$ is 20.5 per cent.

The elimination of hydrogen chloride from the hydrochloride, by means of heat and organic bases, was later more thoroughly investigated by Harries.[142] In order to remove the hydrogen chloride, he heated the hydrochloride *in vacuo* at 100° C. and obtained a product which contained about 12.5 per cent chlorine and retained it very tenaciously. The uniformity of this substance is questionable. Weber's assumption that he had obtained a uniform product, $C_{10}H_{16}.HCl$, by the partial elimination of hydrogen chloride from the hydrochloride is no longer tenable. A formula $C_{20}H_{32}.HCl$ or $C_{25}H_{40}.HCl$ would correspond to a substance containing 12.5 per cent of chlorine, according to Harries.

Pummerer and Stärk [143] heated the hydrochloride at 100° C. under a pressure of 0.1 mm., and succeeded in bringing about a further evolution of hydrogen chloride. They compared the hydrochlorides of sol- and gel-rubber, which have about the same analytical composition. After heating for 20 days, the hydrochloride of sol-rubber still contained 3.27 per cent chlorine, while the hydrochloride of gel-rubber contained 11.23 per cent chlorine.

[140] *Ber.*, **33**, 779 (1900).
[141] Staudinger assumes that degradation of the dissociative rubber molecule has also taken place.
[142] Harries, "Untersuchungen . . . . . ," p.
[143] Unpublished.

After heating for 10 days longer the chlorine content of the sol-rubber hydrochloride had decreased to only 3.0 per cent, while that of the gel-rubber hydrochloride had decreased to 5.35 per cent.

Harries showed that the hydrogen bromide addition products behave in a similar way. When heated *in vacuo* at 100° C., the bromine content decreases below that expected for the formula $C_{10}H_{16}.HBr$. The complete removal of the halogen acid, which cannot be accomplished by heating in air, succeeds almost quantitatively, according to Harries,[144] if the hydrochloride is heated with pyridine at 125° to 135° C. in a sealed tube. The reaction product is isolated by pouring it into water, and washing it on the mill. In this manner, there is obtained a regenerated product, which contains only 0.1 to 0.3 per cent of chlorine. It is thus practically chlorine-free. This hydrocarbon is called *alpha*-isorubber by Harries, and can be obtained from the hydrochloride in a yield of at least 75 per cent. The decomposition of the ozonide of *alpha*-isorubber has led to important conclusions on the constitution of rubber. (*See* p. 217.)

Hydrobromide

The hydrobromide of rubber which Weber[145] could not prepare, was simultaneously prepared by Harries[146] and by Hinrichsen, Quensell, and Kindscher.[147]

A yield of 94 to 95 per cent of the theoretical quantity of the hydrobromide is obtained by the same method employed for the preparation of the rubber hydrochloride. An elementary analysis points conclusively to the formula $(C_5H_8.HBr)_x$. The hydrobromide is grayish white, gradually turns brown, is tough, soluble in chloroform, and insoluble in alcohol. If the hydrobromide is heated, it begins to evolve hydrogen bromide above 135° C. and decomposes completely around 160° C.

Hydrogen Iodide

The hydro-iodide can be obtained in the same manner, with a yield of 76 per cent of the theoretical amount. The analytical data of Harries again point to a formula, $(C_5H_8.HI)_x$. Shortly after preparation, it forms a white, tough mass, which rapidly turns brown or black and decomposes. It is soluble in benzene and insoluble in alcohol. When heated to 100° C., iodine is liberated, and the decomposition is complete at 125° to 135° C.

In contrast to Harries' work, Hinrichsen, Quensell and Kindscher[148] isolated a hydro-iodide which according to an elementary analysis has the formula $(C_{10}H_{16}.HI)_x$. The rubber hydrocarbon has therefore added only one-half the normal quantity of hydrogen iodide. The method of preparation was essentially the same as that used by Harries, the only difference being that the hydrogen halide was previously dried and the reaction mixture was cooled in an ice bath. The different results obtained by the two investigators can probably be traced to these conditions.

For the sake of completeness, it should be mentioned that Spence and Galletly[149] prepared an addition product of chromyl chloride and rubber. The substance is a dark brown powder, and according to the elementary

[144] *Ber.*, **46**, 733 (1913).
[145] *Ber.*, **33**, 779 (1900).
[146] *Ber.*, **46**, 736 (1913).
[147] *Ber.*, **46**, 1286 (1913).
[148] *Ber.*, **46**, 1286 (1913).
[149] *J. Am. Chem. Soc.*, **33**, 190 (1911).

analysis has the composition, $(C_{10}H_{16}CrO_2Cl)_x$. Water decomposes it with the formation of an aldehyde. Selenium oxychloride also forms an addition product with rubber.* [150]

The substances described above are all of high molecular weight. Decomposition of the rubber molecule has therefore not occurred. The important results of the work on the addition products have shown that the rubber hydrocarbon contains one double bond for each five carbon atoms, that is, for each C_5H_8 group in the molecule. The question arises whether the addition of the hydrohalide has taken place without cyclization, since it has been shown that the action of concentrated sulfuric acid on the rubber hydrocarbon results in extensive cyclization (*see* p. 164). Cyclorubber, according to Staudinger, adds less halogen and halogen acid than does rubber. Staudinger further assumes that the reaction of the halogen acids with rubber at the double bonds is accompanied by dissociation of the molecule at certain linkages between diallyl groups, similar to the dissociation of hexaphenylethane (*cf.* p. 188). In connection with this view, it should be mentioned that a solution of rubber hydrochloride is much less viscous than a solution of rubber.

The Action of Nitrous Acid, Oxides of Nitrogen, Nitrosobenzene, and Tetranitromethane on Rubber

Nitrous Acid and Oxides of Nitrogen

If the oxides of nitrogen are allowed to react on a solution of rubber, nitrogen and oxygen enter the rubber molecule. In addition, degradation of the rubber molecule takes place. The principal investigators in this field are Harries, Weber, and Alexander. The results of these investigators are not in agreement, however.

In a preliminary communication, Harries [151] reported that a yellow amorphous substance, insoluble in acetic acid, is obtained when the gases resulting from the action of nitric acid on arsenic are allowed to bubble through a solution of rubber. If this substance is heated in a melting point tube, it begins to sinter at 90° to 100° C. and decomposes at 130° C. without melting. The values for the molecular weight of this substance in methyl acetate, according to Landsberger's method, vary between 1100 and 1700.

C. O. Weber [152] next reported on the action of dry nitrogen dioxide on solutions of rubber. He is supposed to have obtained a substance of definite composition $(C_{10}H_{16}N_2O_4)_x$, which agrees in properties with the above-described product of Harries. At the beginning of the reaction an amorphous substance separates in the form of cohering crusts which soon change to a coarse-grained powder. If this powder is dissolved in acetone and the acetone solution is allowed to flow into water, the reaction product is obtained as a yellow, fine, flaky mass. Weber's analytical results agree very closely with the theoretical value for the formula, $(C_{10}H_{16}N_2O_4)_x$. The substance is very readily soluble in acetone, slightly less soluble in acetic anhydride and ethyl acetate, and insoluble in alcohol, benzene, carbon disulfide, and ether.

* Translator's Note. An addition product of rubber with thioglycolic acid has been obtained by Holmberg [*Ber.*, **65**, 1349-1354 (1932); *Rubber Chem. Tech.*, **6**, 71 (1933)]. The addition product has a composition, corresponding very closely to the formula $C_5H_8(HSCH_2CO_2H)$. The product is soluble in sodium hydroxide and can be reprecipitated with hydrochloric acid in the form of a white amorphous, plastic mass.

[150] Carl E. Frick, *Chem. News*, **127**, 74 (1923).

[151] *Ber.*, **34**, 2991 (1901).

[152] *Ber.*, **35**, 1947 (1902).

The situation was clarified through later exhaustive investigations by Harries,[153] and the existence of Weber's nitrosite was disproved. Harries showed that the reaction of gaseous nitrous acid on rubber proceeds essentially in two stages, which are dependent on the duration of the action of the nitrous acid. The gas is prepared from arsenic by reaction with dilute nitric acid of specific gravity 1.30, and is dried by passing it over phosphorus pentoxide. Under these conditions the gas consists largely of nitrogen trioxide, N_2O_3.

The primary reaction product, which is formed by the action of nitrous acid on the rubber for a short time, is called "nitrosite A" by Harries. It separates as a light-green colloidal precipitate. After it ceases to form, the solution is allowed to stand for several hours and is then filtered. When dried, the precipitate forms a readily friable fine powder which is insoluble in the usual rubber solvents and in alkali. It dissolves in aniline and in pyridine with decomposition. Heated in a melting point tube, the "nitrosite A" decomposes between 80° and 100° C. The elementary analysis of the substance leads to the conclusion that the nitrosite has the formula $(C_{10}H_{16}N_2O_3)_x$, although the carbon and nitrogen values are low, indicating that oxygen has been added to the molecule.

Calcd. for $(C_{10}H_{16}N_2O_3)_x$:	C, 56.60;	H, 7.55;	N, 13.21
Found:	C, 54.12, 55.37;	H, 7.39, 7.18;	N, 12.01

A secondary reaction product, called "nitrosite C," is formed if the nitrous acid is left in contact with the rubber solution for a longer time. It is distinguished from "nitrosite A" by its solubility. The preparation of "nitrosite C," of definite composition, can be duplicated if the same experimental conditions are maintained. The "nitrosite C" seems to be the final product of the action of the nitrous acid with variable N_2O_3 and N_2O_4 content on the rubber, for if the solution in benzene, which is already saturated with the nitrous acid, is allowed to stand for another day, the solubility of the nitrosite is not changed. The "nitrosite C" is also formed when the insoluble "nitrosite A" is suspended in benzene and is then subjected anew to the action of the nitrous acid. In order to obtain the same product repeatedly, Harries perfected the following procedure:

Two hundred cubic centimeters of thoroughly dry benzene are poured over 5 grams of purified rubber, and the following day a rapid stream of nitrous acid is conducted into the swollen mixture. After standing for 24 hours, the precipitated product becomes soft and a sample obtained by filtering a portion of the solution is soluble in ethyl acetate. The entire precipitate is then pressed, washed with benzene, and dried. The product thus obtained is then dissolved in 50 grams of ethyl acetate, and a stream of nitrous acid is passed into the solution at ordinary temperatures until the solution is saturated with the gas. After the reaction mixture has stood for one day, the greater part of the ethyl acetate is evaporated *in vacuo* at 30° C., and the residue is poured into about 400 cc. of absolute ether. When using this method, Harries always obtained the same preparation from the most diverse rubber samples.

A product reprecipitated three times from ethyl acetate with ether, according to the process described above, gave the following analytical figures:

Calcd. for $(C_{10}H_{15}N_3O_7)_x$:	C = 41.52;	H = 5.19;	N = 14.35
Found:	C = 41.65, 40.56;	H = 5.71, 5.58;	N = 14.38

[153] *Ber.*, **35**, 3261, 3263, 4429 (1902).

Molecular weight determinations, by the Landsberger method, gave a value of 561, while the calculated value for the formula $(C_{10}H_{15}N_3O_7)_2$ is 578. The decomposition point of the pure nitrosite C lies between 150° and 160° C. It is a yellow powder which is easily soluble in ethyl acetate and acetone, but is not soluble in alkali without decomposition. With sodium alcoholate it forms a solid sodium salt, which is not converted into the original material by acidification. Nitrosite C readily reduces Fehling's solution. According to a method proposed by Harries, this substance can be used for the quantitative determination of the rubber in commercial mixtures. The applicability of this method to the quantitative determination of rubber has been the subject for lively discussions, and the procedure originally proposed by Harries has suffered numerous changes by others. The lengthy nitrosite method was never permanently adopted as a standard in the technical analysis of rubber. (For details of the method *see* p. 354.)

The previously described nitro compound of Weber $(C_{10}H_{16}N_2O_4)_x$, possesses properties very similar to those of the nitrosite C of Harries.

Fendler [154] and Alexander [155] suggested that the reaction products of rubber with nitrogen dioxide and nitrogen trioxide, respectively, are probably identical. The systematic investigations of Harries [156] elucidated the relationship. He found that the nitro compound, when prepared with nitrogen dioxide, according to Weber's directions, is very similar in properties to the product obtained by Weber $(C_{10}H_{16}N_2O_4)_x$. The analytical results do not agree with his formula, however, in spite of the greatest care in following the directions of Weber. It can be shown that the action of nitrogen dioxide on a solution of rubber proceeds in two stages. The product, immediately after its preparation, is almost insoluble in ethyl acetate, alcohol, acetone, and chloroform. When dry, it forms a golden-yellow powder which begins to decompose at 90° C. Analytical results agreeing with the composition of this product could not be obtained by Harries. If the substance is left in contact with the reaction mixture for one hour after precipitation it becomes completely soluble in ethyl acetate and acetone, and then possesses the properties described by Weber. By reprecipitating this nitrosite from an acetone solution with benzene, Harries succeeded in raising its decomposition point to that corresponding to nitrosite C. An elementary analysis, however, indicates nitrosite C, rather than a substance of the formula $(C_{10}H_{16}N_2O_4)_x$.

Considerable analogy exists between the reaction products of nitrogen trioxide and nitrogen dioxide on rubber. It is very probable that the final products in both cases are identical; namely, Harries' nitrosite C. When pure nitrogen dioxide is used, however, it is more difficult to prepare homogeneous substances of constant composition repeatedly. Harries [157] originally believed that a third nitrosite, namely nitrosite B, was present in the mixture. The evidence for the existence of this substance was based on erroneous conclusions and it must therefore be deleted from the literature.

P. Alexander, in the course of his investigation, obtained results which contradicted those obtained by Harries. Alexander believed that there is present in the reaction product resulting from the action of nitrous acid on rubber, a nitrosite of the formula $(C_9H_{12}N_2O_6)_x$. The properties of this substance are in agreement with those of the nitrosite C of Harries. Its

[154] *Ber. deut. pharm. Ges.*, **15**, 31 (1904); *Gummi-Ztg.*, **18**, 829, 848 (1904).
[155] *Gummi-Ztg.*, **18**, 789, 867 (1904), also *Ber.*, **38**, 181 (1905); *Z. angew. Chem.*, **18**, 164 (1905); **20**, 1355 (1907).
[156] *Ber.*, **38**, 87 (1905).
[157] Harries, "Untersuchungen . . . . . ," p. 30.

decomposition point, according to Alexander,[158] lies between 90° and 100° C. He demonstrated that carbon dioxide was liberated in the preparation of the nitrosite, and believed therefore that he had obtained sufficient proof for his formula. The average results of his analyses are as follows:

Calcd. for $(C_9H_{12}N_2O_6)_x$: C, 44.30; H, 5.37; N, 11.78
Found: C, 44.20; H, 4.92; N, 11.47

It is to be emphasized that Alexander worked under experimental conditions differing from those employed by Harries. Alexander's starting material was not chemically purified rubber, and he did not purify the reaction product by reprecipitation. This explains the different analytical values and the lower decomposition point of Alexander's product. Harries [159] showed quantitatively that when carbon dioxide is eliminated, the loss in carbon never exceeds 0.4 per cent of the total weight of the carbon in the nitro compound. If the elimination of carbon dioxide had taken place according to the equation $C_{10}\ldots = C_9\ldots + CO_2$ the loss would have been almost 9 per cent. Recently, F. Emden [160] investigated the action of nitrogen dioxide on rubber, and despite great care in conducting the reaction in the cold, could not obtain a simple addition product. He obtained a nitrosite which contains more oxygen than Harries' compound, and which corresponds to the formula $(C_{10}H_{10}N_2O_6)_x$. Nitrogen dioxide, therefore, acts as an oxidizing agent. This action is not surprising in view of the relation of its constitution to that of ozone.

Gorgas* [*Ber.*, **63**, 2700 (1930); *Chem. Abstracts*, **25**, 2328 (1931)], repeated the work of previous investigators on the action of the oxides of nitrogen on rubber. He used total rubber carefully purified according to the method of Pummerer and Pahl, and took special precautions to purify the oxides of nitrogen. He found contrary to the other investigators that no homogeneous substances could be obtained by the action of the oxides of nitrogen on rubber, and that a definite formula could not be assigned to the product of the reaction. The reaction of rubber with nitrogen tetroxide was conducted in carbon tetrachloride solution at 0° C. One part of a one per cent solution of rubber in carbon tetrachloride was added to five parts of a solution of N_2O_4 in CCl_4. When the reaction was allowed to proceed for 15 minutes, the resulting product had a composition corresponding only approximately to the formula $C_7H_{10}N_2O_5$. Longer time of reaction gave a product the analysis of which indicated partial oxidation.

The reaction of rubber with nitric oxide was also studied. A 0.3 per cent solution of rubber in CCl_4 at 20° C. was treated for 4 hours with a stream of NO gas. The product was insoluble in acetone and benzene but soluble in aniline and nitrobenzene. Analysis of the product indicated extensive oxidation.

It is stated that a product containing no nitrogen can be obtained by allowing rubber to react with dilute nitric acid to which urea has been added in order to prevent the formation of nitrous acid.

Harries [161] attempted to decompose nitrosite C, in order to obtain proof for the constitution of the nitrosite. He oxidized the nitrosite with a two per cent permanganate solution and obtained principally oxalic acid and succinic acid.

With warm nitric acid of specific gravity 1.4, Harries again obtained oxalic acid as the decomposition product and a light yellow oil as a by-product. This oil is readily soluble in water. Silver nitrate precipitates a difficultly soluble silver salt. Harries considers the oil to be an aliphatic nitro-acid. No definite conclusions about the constitution of nitrosite C could be drawn by Harries from the results of the oxidative decomposition.

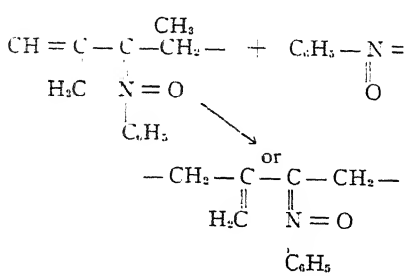
[158] *Gummi-Ztg.*, **21**, 727 (1907); also **25**, 1109 (1911).
[159] Harries, "Untersuchungen . . . . . ," p. 41.
[160] *Ber.*, **58**, 2524 (1925).
* Translator's Note.
[161] *Ber.*, **35**, 3262 (1902).

The action* of [illegible]syl chloride on rubber in benzene solution is recorded by C. O. Weber [illegible]8 (1902); Dubosc and Luttringer, "Rubber, Its Production, [illegible]s," p. 179, Griffin & Co., London, **1918**]. He treated a ben- with iso-amylnitrite and acetyl chloride and found that after solution had set to a gel. Harries, (Abderhalden, "Handbuch der [illegible]smethoden," p. 147, part 10, No. 1, chapter on "Rubber and Lichens," by [illegible], passed nitrosyl chloride into a benzene solution of rubber and obte which contained the calculated quantity of nitrogen and chlorine, the addition product of rubber with nitrosyl chloride. The addition product according to Harries, was partially oxidized by nitrous oxides contained in the nitrosyl chloride.

Nitrosobenzene and other Aromatic Nitroso Compounds

G. Bruni and E. Geiger [162] have recently resumed the earlier experiments of Angeli, Alessandri and Pegna,[163] of Alessandri [164] and of Bruni,[165] and have investigated the action of aromatic nitroso compounds on rubber, with [illegible]s.

work with nitrosobenzene led only to a substance of the formula $C_{55}H_{81}N_5O_9$. Recently, it was established that for every isoprene group in the molecule, one nitroso group enters the molecule. Actually, however, three molecules of the nitroso compound react with each C_5H_8 group when the benzene solution of rubber is warmed for 15 minutes with the reagent. The green solution gradually turns yellow and finally brownish red. After cooling the solution and pouring it into petroleum ether, a substance of the composition, $(C_{11}H_{11}ON)_x$, separates in the form of yellow flakes, having a decomposition point of 135°-140° C. Ninety-four to ninety-eight per cent of the theoretical yield is obtained. One nitrosobenzene molecule has therefore reacted with a C_5H_8 group with the evolution of 2 atoms of hydrogen. The hydrogen reduces a second molecule of nitrosobenzene to phenylhydroxylamine, which reacts with a third molecule of nitrosobenzene to give azoxybenzene. This was isolated from the mother liquor. The resulting rubber derivative is considered a nitrone of isorubber.[166]



The nitrone reacts with bromine to give a dibromide, showing that the nitrone contains one double bond for each C_5H_8 group. X-ray analysis shows that rubber nitrone is an amorphous substance. The nitrone can also be prepared by allowing a pyridine solution of nitrosobenzene to act upon latex diluted with pyridine. The product thus prepared differs slightly in solubility from

* Translator's Note.

[162] *Atti accad. Lincei*, (6), **5**, 823 (1927); *Kautschuk*, **3**, 350 (1927).

[163] *Atti accad. Lincei*, (5), **19**, I, 650 (1910); *Chem. Zentr.*, **81**, II, 302 (1910).

[164] *Atti accad. Lincei*, (5), **24**, I, 62 (1915); *Chem. Zentr.*, **86**, I, 1210 (1915).

[165] *Atti accad. Lincei*, (5), **30**, I, 337 (1921); *Chem. Zentr.*, **93**, II, 259 (1922).

[166] See also *Chem. Reviews*, **7**, 107 (1930).

the nitrone prepared by the other method. Analyses of this substance are not recorded.

Reactions were also carried out with ortho-, meta-, and para-nitrosotoluene and with ethyl ortho-nitrosobenzoate and other nitroso bases, but nitrosophenol does not react with rubber. The corresponding acid of the ethyl ortho-nitrosobenzoate addition product was prepared by saponification of the ester addition product. The solution of the acid exhibits colloidal properties.

Phenylhydrazine reacts with the nitrone of rubber by displacing the nitrosobenzene group and forming a phenylhydrazone derivative of rubber. The phenylhydrazone derivative is probably produced from the ketone of rubber (caoutchone). Further investigation of these derivatives should lead to aminorubber and to the introduction of a ketone group in the rubber molecule.

Pummerer and W. Gündel [167] used the nitrosobenzene reaction to determine possible differences in the individual rubber fractions. In the course of their investigation they established conclusively that one nitrosobenzene molecule enters into reaction with one isoprene group. In the reaction of rubber with nitrosobenzene, it is difficult to prevent the absorption of a small amount of oxygen. This always occurs when the usual directions of Bruni and Geiger for the preparation of nitroso compounds (heating for fifteen minutes on the water bath) are followed. The reaction with nitrosobenzene is best conducted by working with a cold concentrated benzene solution of rubber. Under these conditions, it is noticeable that the original highly viscous solution becomes thinly fluid in a short time (20 to 30 minutes). The reaction conducted in an atmosphere of carbon dioxide, requires about one to two days, depending on the temperature. The yellow reaction product is precipitated with petroleum ether, filtered, washed with petroleum ether, and dried (with exclusion of air) in a high vacuum. In view of the noticeable change in viscosity, it was somewhat questionable whether the rubber nitrone possessed the highly colloidal nature mentioned by previous investigators. Pummerer and Gündel therefore determined the molecular weight of the nitrone in benzene and in nitrobenzene. These determinations showed that the rubber nitrone possesses an average molecular weight of 1200 to 1400. The nitrone, as in the case of rubber, is probably a mixture of closely related substances. On an average, eight isoprene groups are combined with eight molecules of nitrosobenzene, which gives a nitrone molecule having a molecular weight of 1384. The molecular weight of the nitrone, therefore, does not point to a very large rubber molecule. In this connection, it is interesting to note that the nitrone of gutta-percha is composed, on an average, of 6 isoprene groups plus 6 nitrosobenzene groups.[168]

It is noteworthy that analytically pure rubber nitrone prepared by the method of Pummerer and Gündel is completely soluble in benzene. The fact that the solubility in benzene decreases on aging, recalls the solubility changes of rubber on storing. The slightly oxidized nitrones of rubber which are usually produced during the reaction of rubber with nitrosobenzene and are always formed when the mixture is heated, contain portions which are insoluble in benzene from the beginning. The oxidized nitrones are completely soluble in nitrobenzene, however, and in this solvent have an average molecular weight of 1200 to 1400. The molecular weight cannot be determined immediately after the last of the solid has dissolved, or else values 1000 to

[167] *Ber.*, **61**, 1591 (1928).

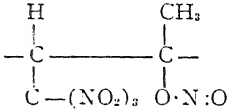
[168] Pummerer and H. Brunswig, unpublished; see also Staudinger and Joseph, *Ber.*, **63**, 2898 (1930); *Rubber Chem. Tech.*, **4**, 198 (1931).

2000 higher than those given above may be obtained, which are probably due to incomplete solution of the micelles. After one to two hours, the change is complete in all cases, and the final state may be regarded as a molecular dispersion.

Tetranitromethane

Tetranitromethane, according to A. Werner [169] and J. Ostromislensky [170] serves as a reagent for the determination of olefinic double bonds, since it gives yellow unstable addition products with unsaturated hydrocarbons.

Pummerer and Pahl [171] showed that the formation of a yellow compound can be observed when solid rubber is added to pure tetranitromethane. If the reaction is carried out in hexahydrotoluene solution, the reaction mixture first turns yellow. After five or six days (at 0° C.) the solution is decolorized and an almost colorless or only faintly yellow or pink stable addition product separates. It does not lose tetranitromethane, even when dried in a high vacuum for six hours at 60° C. The tetranitromethane is apparently bound to the rubber by primary valences. The tetranitromethanate probably has the following formula:



It is possible that the nitro groups through their auxiliary valences, block other double bonds of the rubber molecule. It is peculiar that here for the first time not all of the double bonds of the rubber molecule react with a reagent for olefin double bonds. One tetranitromethane molecule reacts with every 4 to 6 isoprene groups if the reaction is carried out at 0° C. in hexahydrotoluene. All analytical results thus far obtained indicate that the tetranitromethane and not nitrogen oxides have combined with the rubber.

If one of the usual commercial varieties of crude rubber, such as crepe or smoked sheets, or alkali-purified rubber, is used, a ratio of 1 to 5 for tetranitromethane to C_5H_8 is obtained. It is remarkable how widely the ratio varies with different varieties of rubber, and even with the same rubber when solutions of rubber of different concentrations are used in the preparation of the tetranitromethanate. Even colloidal chemical factors such as the previous history of the solution of rubber seem to have an influence. In several cases where concentrated solutions of pure rubber had originally been prepared, tetranitromethanates of total rubber were obtained which gave higher ratios for the addition of tetranitromethane to C_5H_8 groups, namely 1 to 4. The tetranitromethanate when suspended in an inert solvent, still decolorizes bromine. The yields of the tetranitromethanate correspond to 90 to 95 per cent of the theoretical amount.[172]

The tetranitromethanates prepared at 0° C. are fine powders, insoluble in all of the common organic solvents in the cold, and are non-crystalline, according to the x-ray work of Dr. Rosbaud. When the substance is heated to 150° C. in a tube it begins to turn yellow, becomes brown at 175° C., and finally carbonizes. On a copper block, it explodes at 160° to 170° C. For this reason copper oxide mixture is always used in the analysis of the com-

[169] *Ber.*, **42**, 4324 (1909).

[170] *Ber.*, **43**, 197 (1910).

[171] *Ber.*, **60**, 2152 (1927); *Rubber Chem. Tech.*, **1**, 167 (1928).

[172] H. Pahl, Dissertation, Erlangen, **1926.**

pound. The temperature of the reaction between rubber and tetranitromethane can be raised to 75° C. without essentially changing the results. Above 50° C., oxides of nitrogen are formed.

Behavior of Rubber Toward Oxidizing Agents

Various Oxidizing Agents

Behavior toward Air

E. Herbst [173] treated solutions of rubber in aromatic hydrocarbons with air and, after evaporation of the solvent, isolated two distinctly different substances, which differed from the original material, and to which he ascribed the formulas $C_{10}H_{16}O$ and $C_{10}H_{16}O_3$.

Peachy [174] studied the rate of absorption of oxygen by rubber quantitatively by allowing a measured quantity of pure oxygen gas to react on rubber. He proved that one atom of oxygen is consumed for each C_5H_8 group. He found that the rate of reaction was 20 to 30 times greater when de-resinified rubber was used than when rubber containing the resins was employed. Similar experiments were carried on by Pummerer and Burkard,[175] who worked with rubber which was purified according to the method of Harries. They showed also that in very dilute hexahydrotoluene solutions one atom of oxygen was absorbed for each C_5H_8 group. In very concentrated solutions, however, the amount of oxygen absorbed was much less.

F. Kirchhof [176] exposed crude rubber to the action of light and air for one year, and showed that in the oxidation of rubber, peroxides were formed. Peroxides were also formed when thin strips of rubber were suspended in a 3 per cent solution of hydrogen peroxide. Kirchhof considered that these peroxides were the unstable primary products of oxidation, and that they were then changed into the final stable product.

Weil [177] showed by means of the pyrrole test that levulinic aldehyde, which was produced by auto-oxidation, was present on the surface of balls of crude rubber.

Behavior toward Permanganate

It is characteristic of the double bond in the rubber molecule that it reacts relatively slowly with a solution of permanganate in sodium hydroxide, the well known reagent for the oxidation of olefin double bonds.

Harries [178] allowed 2 grams of rubber, dissolved in 200 cc. of benzene, to react with a solution of permanganate containing 3.1 grams of permanganate in 150 cc. of water. After shaking the mixture continuously for about 30 hours, the permanganate was all consumed. After evaporation of the benzene from the solution, a thick colorless syrup remained, the elementary analysis of which pointed unexpectedly to the unchanged hydrocarbon $(C_5H_8)_x$. Only the solubility and the appearance of the rubber were changed, causing Harries to regard the rubber, which was treated with permanganate, as being depolymerized. Small quantities of a fatty acid were found in the water solution. The permanganate which was consumed, therefore, attacked only a small part of the rubber employed, but oxidized it more thoroughly.

[173] *Ber.*, **39**, 523 (1906).
[174] *India Rubber J.*, **45**, 8 (1913); *J. Soc. Chem. Ind.*, **31**, 1103 (1912).
[175] *Ber.*, **55**, 3465 (1922).
[176] *Kolloid-Z.*, **13**, 49 (1913).
[177] Harries, "Untersuchungen . . . . . ," p. 50.
[178] *Ber.*, **37**, 2708 (1904).

Thoroughly milled rubber reacts with permanganate more readily. The quantity of permanganate consumed in this case is also small in proportion to the amount added. The reaction products are in no way different from those obtained by treating rubber which has not been mechanically worked.

Van Rossem and van Heurn [179] confirmed the results of Harries, and showed further that the viscosities of solutions of rubber are greatly lowered by treatment with permanganate.

Rubber which had been treated with permanganate solution for a long time, was ozonized by Harries.[180] The ozonides were somewhat more fluid than those obtained from normal rubber, and after decomposition of the ozonide, gave a less definite pyrrole test. High-vacuum distillation of rubber, previously treated with permanganate, added nothing new to the existing knowledge.

Recently Staudinger [181] resumed work on the oxidation with permanganate, and stated that the rubber hydrocarbon reacted less sluggishly with acid permanganate solution. The results of these experiments have not been published.

Robertson and Mair* [*J. Soc. Chem. Ind.*, **46**, 41T (1927); see also, Mair and Todd, *J. Chem. Soc.*, **1932**, 386] also studied the action of potassium permanganate solution on rubber. The products obtained in neutral or alkaline solutions are insoluble in ethyl alcohol and acetone, and vary from pale yellow, slightly elastic substances, to white brittle resins, depending on the oxygen content of the product. Among the acidic products of the oxidation are found formic, acetic, oxalic and levulinic acids, and colloidal resinous substances. They also oxidized rubber with hydrogen peroxide and with chromyl chloride. The former yielded a product of the average composition $C_{50}H_{102}O_{16}$. The oxidation with chromyl chloride yielded two products, a resin with aldehyde properties, and complex substances containing both chromium and chlorine. The results of the investigation lead to the conclusion that the rubber molecule is very complex and has a high molecular weight. The simplest oxidation product contains at least 40 carbon atoms. In the latest work on the oxidation of rubber by hydrogen peroxide, Mair and Todd have obtained a substance, alcoholic in character, corresponding to the empirical formula $C_{20}H_{36}(OH)_{16}$.

Behavior toward Nitric Acid

Concentrated nitric acid attacks rubber energetically, with the formation of red fumes. If the resulting solution is poured into water, a yellow substance is precipitated, according to Ditmar.[182] Analyses and molecular weight determinations indicate that the product is probably a dinitro derivative of dihydro- or tetrahydrocumic acid and possesses the formula $C_{10}H_{12}N_2O_6$. By carefully evaporating the mother liquor, Harries [183] isolated a light yellowish oil as the main product of the reaction. From the oil he separated oxalic acid quantitatively by means of ethyl acetate. The quantity of oxalic acid produced corresponded to a ratio of two carbon atoms to each $C_{10}H_{16}$ complex. The oil itself yielded difficultly soluble yellow silver salts of unknown constitution. The starting material could be recovered from these salts by neutralization with hydrochloric acid.

A product* similar in appearance to that obtained by Ditmar was prepared by Terry, [*J. Soc. Chem. Ind.*, **11**, 970 (1892)] who allowed dilute nitric acid to react on sheet rubber for a period of six weeks. Fisher [184] obtained a different product by allowing nitric acid to react on a solution of rubber in carbon tetrachloride. A 5 per cent solution of rubber and concentrated nitric acid were used and the yield was practically quantitative

[179] *Kolloidchem. Beihefte*, **10**, 9 (1918).
[180] Harries, "Untersuchungen . . . . . ," p. 51.
[181] *Ber.*, **57**, 1204 (1924), Footnote.
[182] *Ber.*, **35**, 1401 (1902).
[183] *Ber.*, **35**, 3265 (1902).
* Translator's Note.
[184] U. S. Pat. 1,609,806 (1926); and note in *Ind. Eng. Chem.*, **19**, 1333 (1927); *Chem. Reviews*, **7**, 111 (1930).

for a substance having the formula $(C_5H_7NO_2)_x$. The substance is insoluble in sodium carbonate solution, whereas Ditmar's product is soluble in this reagent. The new substance decomposes spontaneously at room temperature and explodes when heated. Fisher is of the opinion that the product is probably a nitropolycyclo-rubber.

Behavior toward Perbenzoic Acid and Other Peroxides

Pummerer and Burkard [185] studied the action of perbenzoic acid on a solution of rubber in chloroform. They studied the progress of the reaction by means of titration, and showed that one atom of oxygen is rapidly absorbed for each C_5H_8 group. The product of the reaction is a white substance, insoluble in the usual solvents for rubber. The analytical figures correspond to those calculated for the formula $(C_5H_8O)_x$.

Weber [186] investigated the oxidation of rubber with chromic acid, peroxides, and persulfates. The reaction products are substances soluble in alcohol, concerning the nature of which nothing further is known.

Recently Boswell [187] allowed various oxidizing agents, such as potassium permanganate, hydrogen peroxide, and iodine to react on rubber. A 7 per cent solution of permanganate was shaken for five days with a 4 per cent carbon tetrachloride solution of rubber. The results of elementary analyses of the oxidation product which was precipitated with methyl alcohol agreed well with the empirical formula $C_{25}H_{40}O$. This substance rapidly absorbs oxygen from the air and then corresponds to the formula $C_{25}H_{40}O_2$. Similarly, with hydrogen peroxide, Boswell obtained oxidation products which on analysis indicated the formulae $C_{30}H_{48}O$, $C_{25}H_{40}O_2$, and $C_{15}H_{24}O$. If iodine was present in the reaction between hydrogen peroxide and rubber, a compound of the formula $C_{25}H_{48}O_8I$ was obtained.

On the basis of these experiments, Boswell arrived at a formula containing multiple ring structures but no double bonds. This view, however, is not shared by others, for the reaction products of rubber with the halogens and halogen acids, and especially with perbenzoic acid, clearly show that one double bond enters into reaction for each C_5H_8 group. These reactions, however, give no further information about the constitution of rubber. The work on the degradation of rubber and of isorubber by ozone, which has been conducted by Harries with great success since 1904, has greatly advanced our knowledge of the constitution of rubber.

The importance* of the role that oxygen plays during the milling of rubber has only recently been recognized. The idea that the breakdown of rubber during milling is chemical in nature and is caused by oxygen was suggested by Fisher and Gray [*Ind. Eng. Chem.*, **18**, 414-416 (1926)]. They found that milling caused an appreciable number of double bonds to become saturated and attributed this fact to oxidation.

Fry and Porritt [*Trans. Inst. Rubber Ind.*, **3**, 203-216 (1927)] showed that the plasticizing effect of milling on rubber can also be produced by oxidizing the rubber with heat, but without mechanical action.

Park, Carson, and Sebrell [*Ind. Eng. Chem.*, **20**, 478-84 (1928)] found that a permanently softened rubber could be obtained by heating rubber. Grenquist [*Ind. Eng. Chem.*, **22**, 759-65 (1930)] showed that breakdown analogous to that brought about by milling could be brought about by heating rubber in air.

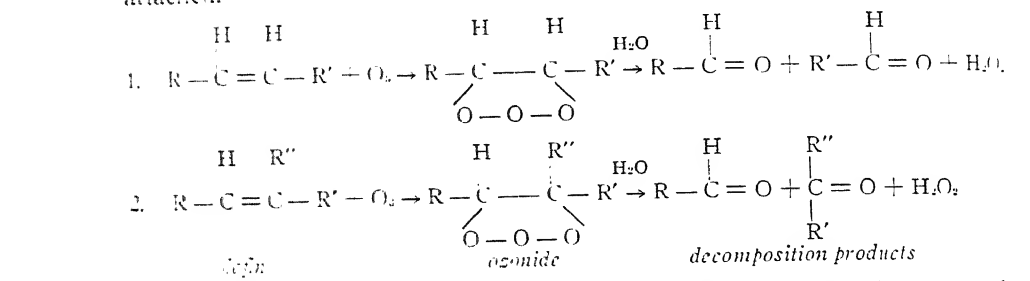
Shacklock [*Trans. Inst. Rubber Ind.*, **6**, 259 (1930)] showed by means of surface tension measurements on rubber solutions, that a new compound was formed from rubber by milling it in air. He assumed that this compound was formed by oxidation. He also showed [*Trans. Inst. Rubber Ind.*, **7**, 354-65 (1932)] that the acetone extract of masticated rubber increased during milling. This increase was assumed to be due to oxidation products of the rubber.

[185] *Ber.*, **55**, 3462 (1922); **62**, 2636 (1930).
[186] Weber, C. O., "The Chemistry of India Rubber," p. 40, Griffin & Co., London, **1902.**
[187] *India Rubber J.*, **64**, 981 (1922).
* Translator's Note.

Cotton [*Trans. Inst. Rubber Ind.*, **6**, 487-515 (1931)] and also Busse [*Ind. Eng. Chem.*, **24**, 140-146 (1932)] showed very conclusively that oxygen is necessary for the plasticizing of rubber during mastication. By milling rubber in nitrogen the above investigators showed that the rate of breakdown was much slower when little or no oxygen was present. Cotton also showed that rubber gained in weight during milling in spite of the loss of volatile oxidation products. Busse demonstrated that peroxides which are formed during autoxidation of unsaturated compounds are also formed during the milling of rubber. These peroxides were detected by means of their action on a photographic plate. Types of rubber which broke down more slowly during milling (spray dried latex and fine Para) did not give a photographic test for peroxides. The intensities of the peroxide tests were directly proportional to the ease of breakdown during milling.

Ozone Degradation of Rubber

Harries,[188] through his extensive investigations, clarified the mechanism of the action of ozone on unsaturated hydrocarbons. He showed that one molecule of ozone attaches itself to each double bond of an olefin to give usually, amorphous, sometimes explosive, viscous substances called ozonides. On warming with water, these substances decompose into aldehydes and hydrogen peroxide, or ketones and hydrogen peroxide, according to whether the carbon atoms of the ethylene group have hydrogen or alkyl groups attached.



The investigations of Harries on the decomposition of rubber by means of ozone,[189] have greatly extended our knowledge of the chemistry of rubber.

Preparation of the Ozonide

When rubber is to be treated with ozone, it is first allowed to swell in a solvent which is itself only slightly attacked by the gas. For this purpose, ethyl acetate and chloroform are especially suited, although the latter is slightly decomposed by ozone with the formation of phosgene and hydrogen chloride. The solution of rubber is then treated with a stream of oxygen containing ozone.

Two different ozonides are produced, depending on the concentration of ozone in the gas. With oxygen gas containing 6 per cent of ozone, a normal ozonide $(C_5H_8O_3)_x$ is formed. If the oxygen contains 12 per cent of ozone or more, there is formed a substance of the formula $(C_5H_8O_4)_x$ which Harries termed oxozonide. E. H. Riesenfeld[190] has recently shown that oxozone, which Harries denoted by the formula O_4, does not exist. The name oxozonide has, however, been retained.

[188] Compare *Ann.*, **343**, 311 (1905); *Ber.*, **42**, [illegible]; *Ann.*, **374**, 288 (1910); *Ber.*, **45**, 936 (1912); also E. Fonrobert, "Das Ozon," Enke, Stuttgart, **1916**.

[189] Harries, *Ber.*, **37**, 2708 (1904); *Ber.*, **38**, 1199 (1905), also "Untersuchungen," p. 51 ff.

[190] E. H. Riesenfeld and G. M. Schwab, *Ber.*, **55**, 2088 (1922); *Naturwissenschaften*, **10**, 470 (1922); *Z. Physik*, **11**, 12 (1922); *Z. Elektrochem.*, **29**, 119 (1923).

The normal ozonide of rubber, $(C_5H_8O_3)_x$ is obtained by following the directions given below:[191]

Ten grams of rubber are allowed to swell in 120 cc. of chloroform for 24 hours, and a stream of gas containing 6 per cent of ozone, previously washed by passing through sodium hydroxide and then sulfuric acid, is passed into the rubber solution. The end of the reaction is recognized when a sample no longer decolorizes bromine. After evaporating the solvent *in vacuo*, the residue (the yield of the crude ozonide is quantitative) is dissolved in ethyl acetate and is purified by reprecipitation with petroleum ether. The oily ozonide sometimes solidifies in the vacuum desiccator to a glassy mass, and in this state is explosive and melts at 50° C. The yield of the pure ozonide amounts to 80 per cent of the theoretical yield. Results of an elementary analysis agree very well with the formula $(C_5H_8O_3)_x$.

Calcd. for $(C_5H_8O_3)_x$: C, 51.72; H, 6.90
Found: C, 51.66; 51.73; 52.19. H, 7.66; 7.59; 7.16

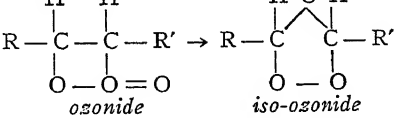
Molecular weight determinations did not give consistent results. Determinations in acetic acid, according to the cryoscopic method, gave values of 230, whereas 232 is the calculated value for the formula $(C_5H_8O_3)_2$. If benzene is used as a solvent, the values agree with the formula $(C_5H_8O_3)_5$; calculated 580; found 535. Harries considers the value found in benzene solution as the more likely of the two, and believes that the low value obtained in acetic acid is the result of the decomposition of the ozonide. For this reason, these determinations no longer have any significance.

The ozonide $(C_5H_8O_4)_x$ is similarly obtained by the use of a current of unwashed 12 per cent ozone. The yield, after purification, is somewhat smaller than is obtained with the normal ozonide. The ozonide is also more readily soluble than the normal ozonide. The product of the reaction is a thick syrup which, in contrast to the normal ozonide, cannot be made to solidify. Since the ozonide decomposes very readily, molecular weight determinations in benzene and acetic acid give even less reliable results. The analysis agrees with the formula $(C_5H_8O_4)_x$, especially if the treatment with 12 per cent ozone is prolonged.

Calcd. for $(C_5H_8O_4)_x$: C, 45.45 H, 6.06
Found: C, 46.84; 46.71; 45.70. H, 6.61; 6.58; 6.12

The material used in obtaining the third values resulted from an experiment in which the treatment with a gas containing a high percentage of ozone was prolonged.

Harries[192] attempted in vain to regenerate the rubber hydrocarbon from the ozonide. Experiments which he carried out toward this end with aluminum amalgam and zinc dust were completely futile. The ozonide is therefore best formulated today, according to Staudinger,[193] by means of bridged oxygen atoms, assuming an immediate rearrangement of the ozonide to the iso-ozonide:



ozonide *iso-ozonide*

[191] Harries, *Ber.*, **37**, 2708 (1904); *Ber.*, **38**, 199 (1905); *Ber.*, **45**, 936 (1912); *Ann.*, **395**, 232 (1913).

[192] Harries, "Untersuchungen . . . . ," p. 64.

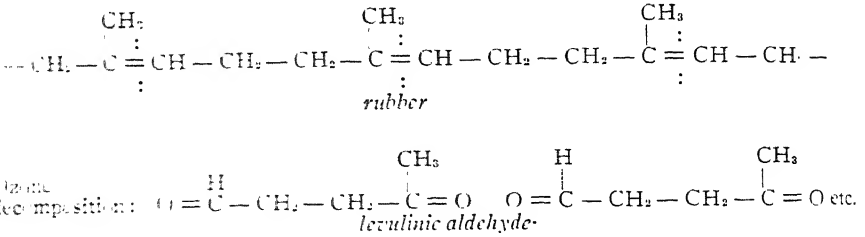
[193] *Ber.*, **58**, 1088 (1925).

This explains why the reduction always yields decomposition products and not glycols or the like.

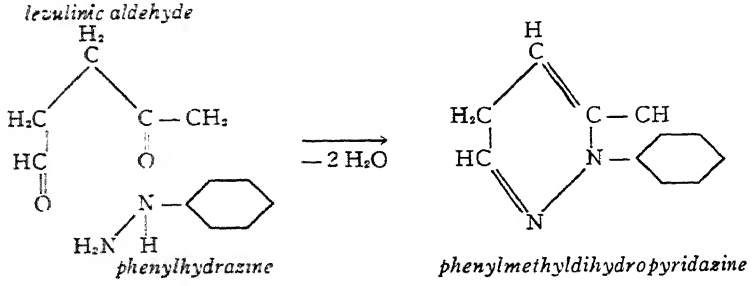
Decomposition of the Ozonides

The decomposition with hot water is by far the most important reaction of the rubber ozonides. In this way the ozonides are almost quantitatively decomposed into derivatives of the unit group C_5H_8; levulinic aldehyde, levulinic acid, and levulinic aldehyde peroxide. In addition, small quantities of carbon dioxide, formic acid and succinic acid are produced. Hydrogen peroxide is formed as a by-product. The decomposition of the ozonides is carried out, according to Harries,[194] by boiling the ozonides with a small amount of water under a reflux condenser, filtering the solution, and distilling *in vacuo*. The aldehydes which are formed in the decomposition are volatile with steam and are found in the distillate, while levulinic acid and the very stable levulinic aldehyde peroxide remain in the residue. In distinction from the aliphatic diterpene ozonides, the decomposition does not take place in the cold upon shaking with water.

Aside from some hydrogen peroxide which is formed by the decomposition of the ozonide, the distillate consists of an aqueous solution of levulinic aldehyde. This aldehyde, since it possesses the carbonyl groups in the 1,4-position, readily reduces Fehling's solution and responds to the pyrrole test. From the structure of the aldehyde it follows that the molecule of rubber contains a recurring double bond after each fourth carbon atom, as represented by the following scheme:



With phenylhydrazine acetate and hydrochloric acid, the levulinic aldehyde forms a light yellow precipitate of phenylmethyldihydropyridazine, which serves to characterize the levulinic aldehyde, and is produced according to the following reaction:



[194] *Ber.*, **37**, 2710 (1904); *Ber.*, **38**, 1200 (1905).

With hydroxylamine, Harries obtained the dioxime of levulinic aldehyde in the form of well defined crystals, having a melting point after recrystallization of about 74° C. Harries prepared the free aldehyde by decomposing the ozonide with a very small quantity of water. From the resulting very concentrated distillate, the aldehyde could be salted out with potassium carbonate. The boiling point of the free aldehyde as determined by Harries, was between 66° and 68° C., at 10 mm. pressure. Other volatile aldehydes and ketones were not obtained, according to Harries. Even with very careful distillation through a fractionating column, no low-boiling constituents were obtained.

The residue obtained after evaporating the solution containing the decomposition products consists, for the most part, of levulinic acid and levulinic aldehyde peroxide. The ratio of the quantities of these two substances to the aldehyde is not constant and varies with the time of action of water on the ozonide. If the water is allowed to remain in contact with the ozonide for a long time, levulinic acid is formed almost exclusively. To isolate the acid, the residue from the distillation of the aldehyde is further concentrated by evaporation *in vacuo,* and the remaining syrup is distilled. The levulinic acid then passes over between 135° and 145° C., at a pressure of 10 mm. The yield, on the average, is about 35 per cent of the theoretical. To characterize it, Harries prepared the phenylhydrazone derivative having a melting point of 108° C.

If a minimum amount of water is used in the treatment of the ozonide and the resulting solution is cooled, crystals of levulinic aldehyde peroxide separate. The levulinic aldehyde peroxide can be recrystallized from water. After recrystallization it melts with decomposition at 197° C.

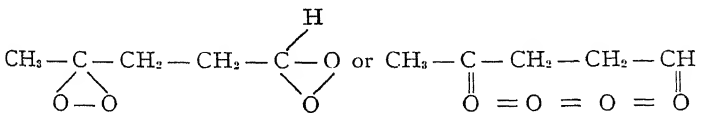
The elementary analysis gave the following values:

Calcd. for $C_5H_8O_4$: C, 45.45 H, 6.06
Found: C, 45.42; 45.32 H, 6.26; 6.63

The results of the molecular weight determination in acetic acid were:

Calcd. for $C_5H_8O_4$: Mol. Wt., 132 Found: 124

The substance possesses the characteristic properties of a peroxide. It is explosive, liberates iodine from potassium iodide solution, and decolorizes indigo solution. It also decolorizes dilute permanganate solution and slowly reduces ammoniacal silver nitrate solution. It dissolves as a weak acid in sodium hydroxide and gives a difficultly soluble silver salt. Since the substance does not react with phenylhydrazine, Harries considered it a normal diperoxide of levulinic aldehyde.



According to this author, the acidic properties of the peroxide can be traced to the hydrogen atom attached to the carbonyl group. This hydrogen atom can be replaced by a CH_3 group by preparing the silver salt and treating with methyl iodide.[195] The resulting compound forms white needles, melting at 102.5° C., soluble in alcohol, benzene, ethyl acetate, and chloroform, and insoluble in petroleum ether.

[195] Harries, "Untersuchungen . . . . . ," p. 59.

By quantitatively determining the amounts of the decomposition products of the ozonide, Harries attempted to show that the cleavage of the ozonide produced mainly the three substances mentioned above. For this purpose, he treated 5 grams of the ozonide with water and obtained the following products:

	I	II
Aldehyde	2.3	2.0
Acid	1.0	1.5
Peroxide and resin	0.7	0.2
Unchanged ozonide	0.5	0.5
Total	4.5 grams	4.2 grams

The levulinic aldehyde formed was determined by treating it with phenylhydrazine and weighing the resulting pyridazine derivative. The yield from 5 grams of ozonide is theoretically 4.3 grams of aldehyde, or 5 grams of levulinic acid. Since the method of determining the aldehyde gives an accuracy of 80 to 90 per cent, Harries' results may be considered fairly satisfactory.

Pummerer * has improved the method of decomposing the ozonide of rubber, and has approached the goal of a quantitative cleavage of the ozonide. Ozonization of the rubber is conducted in chloroform with 3 to 4 per cent ozone. Cleavage of the ozonide is accomplished in moist ether through reduction, either catalytically by the action of platinum black and hydrogen or by means of calcium and oxalic acid or aluminum amalgam. The total yield of cleavage products based on the carbon skeleton of the rubber used, amounts to 95 per cent. The rubber ozonide is at first soluble in chloroform, but after standing deposits considerable quantities of levulinic acid peroxide (from 12 to 20 per cent).

The two per cent of acetic acid which was found in the cleavage products after reduction of the ozonide may originate in an end member of the chain. Small quantities of acetone were detected in the cleavage fragments but their presence is attributed to an impurity [R. Pummerer, G. Ebermayer and K. Gerlach, *Ber.*, **64**, 804, 809 (1931); also, *Kautschuk Chem. Tech.*, **4**, 381, 386 (1931)].

The results of the decomposition of the oxozonide are essentially the same as those obtained with the normal ozonide. On decomposition, the latter yields more aldehyde than acid, while the oxozonide yields more acid than aldehyde. This distinction between the two ozonides is increased with the purity of the ozonides. Harries gives the following figures:

	I. Ozonide $(C_5H_8O_3)_x$	II. Oxozonide $(C_5H_8O_4)_x$
Levulinic aldehyde	4.0	2.8
Levulinic acid	3.0	4.0
Peroxide and resin	2.2	2.2
Total	9.2 grams	9.0 grams

Under item I, 11.6 grams and under item II, 12.9 grams of the ozonide were used. In order to investigate the progress of the decomposition of the ozonide and the products resulting from the decomposition of different varieties of rubber, Harries [196] used a refined method, and directed his attention to the study of the time consumed in the decomposition; that is, the rate of decomposition. The refinement consisted in connecting the decomposition apparatus with absorption vessels in which any volatile constituents were collected. It was possible for Harries, with this improved apparatus, to detect small quantities of carbon monoxide, carbon dioxide, hydrogen, and oxygen.

* Translator's Note.

[196] Harries, "Untersuchungen . . . . . ," p. 59.

The water solution containing the products of decomposition was carefully neutralized with calcium carbonate, and, after filtering, was concentrated *in vacuo* until the residue solidified. The calcium salts of the acids which were contained in the residue were quantitatively separated from any aldehyde by extracting with ether. (Extract I.)

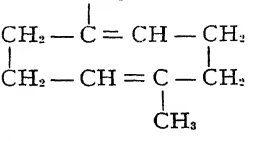
The distillate contains most of the substances which are volatile with steam. It is saturated with salt, and is then extracted 10 to 20 times with ether. (Extract II.) Extracts I and II are then united and, in the case of natural rubber, contain pure levulinic aldehyde.

The calcium salts, containing an average amount of 19 per cent calcium, are carefully decomposed with sulfuric acid and the free acids are quantitatively extracted with ether. On evaporating the ether extracts, the main quantity of the acid remains in the residue. With natural rubber, Harries found, in addition to small quantities of formic acid and succinic acid, mainly levulinic acid and occasionally levulinic aldehyde peroxide. The best yields obtained by Harries [197] [expressed as per cent of $(C_5H_8)_x$] were: 32.94 per cent of crude levulinic aldehyde, 44.1 per cent levulinic acid, 0.56 per cent formic acid, 0.7 per cent succinic acid; the losses were greater than 20 per cent, frequently greater than 30 per cent (*see* p. 236).

The determination of the rate of decomposition of the ozonide, which is especially valuable in the comparison of artificial with natural rubber, was investigated by Harries.[198] He suspended molecular quantities, usually 0.05 mol of the ozonide of normal rubber, in water and gravimetrically compared the amounts decomposed in unit time. The apparatus used by Harries [199] consisted of a flask connected to a reflux condenser and heated in a glycerol bath at a temperature of 120° to 125° C. In Figure 47 are given the decomposition curves of various natural and artificial varieties of rubber. The ordinates represent quantities of ozonide decomposed in grams, and the abscissas corresponding time intervals in minutes.

The decomposition of the ozonide with bromine [200] takes place in the same manner as with water. In this case brominated decomposition products are formed, namely, dibromolevulinic acid and tribromolevulinic aldehyde. If the ozonide is treated in the cold with excess bromine, copious quantities of crystals of dibromolevulinic acid, having a melting point of 114° C., separate after 24 hours. If the ozonide is allowed to stand for 48 hours, with an excess of bromine, in the absence of moisture there results a reddish-yellow oil which was identified by Harries as tribromolevulinic aldehyde.

After the conclusion of this work, the results of which were so simple yet so important for the determination of the constitution of rubber, Harries proposed an eight-membered ring formula for the fundamental unit of the rubber hydrocarbon,



the 1,5-dimethylcyclo-octadiene.

[197] Harries, "Untersuchungen . . . . . ," pp. 60, 62, 116.
[198] *Ber.*, **41**, 3553 (1908).
[199] Harries, Danzig lecture, see "Untersuchungen . . . . . ," p. 222.
[200] Harries, "Untersuchungen . . . . . ," p. 65.

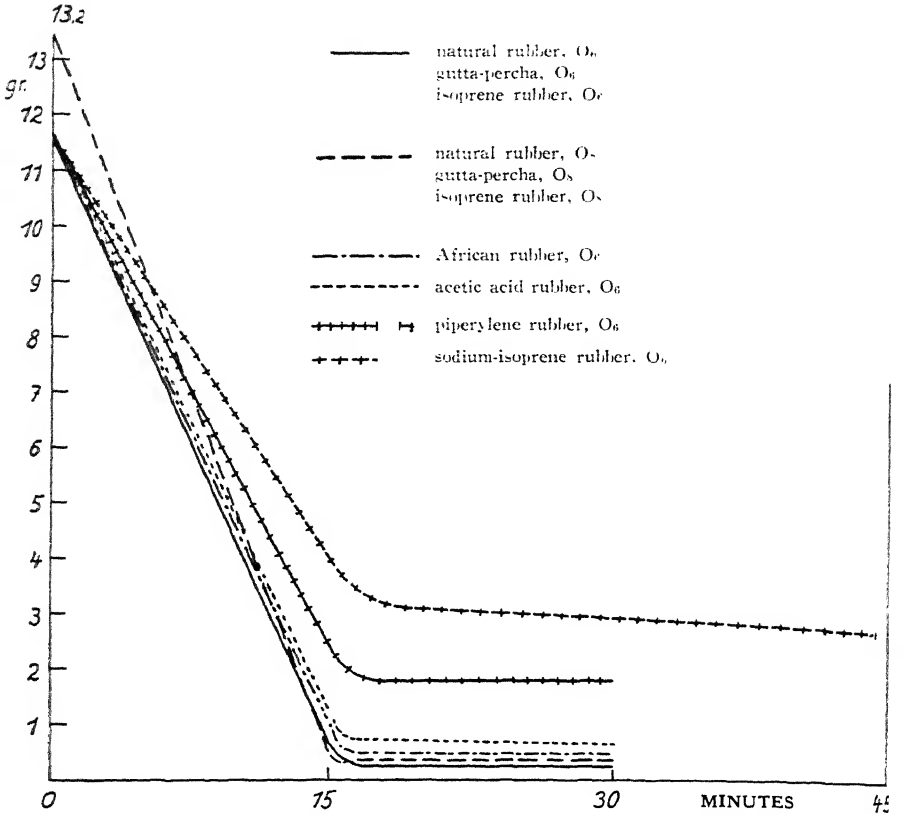


Figure 47—Rates of decomposition of the ozonides of natural and artificial rubbers (according to Harries).

The highly colloidal form of rubber, according to Harries' view, is therefore produced by the coupling of a great number of such fundamental units by means of secondary valences. The formula readily explains the formation of the ozone degradation products and the addition reactions of the halogens and halogen acids. The formula was generally accepted, when Harries compared the ozonide of synthetic butadiene rubber (*see* p. 260) with the ozonide of 1,5-cyclo-octadiene prepared by Willstäter, and found that all of their properties and even their rates of decomposition with water, were very similar. The problem of determining the constitution of rubber seemed to be solved.

This conclusion was, however, false. In 1907 Harries[201] himself pointed out that the constant recurrence of the group $-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$ (isopentene group) in a large ring structure, composed of four or more

[201] Harries, Danzig address.

isoprene groups, was also in accord with his results on the ozone degradation. A very different viewpoint was developed by Pickles,[202] who suggested a ring structure composed of many isopentene groups. In 1914 Harries himself abandoned the cyclo-octadiene formula as a result of his investigations on the decomposition of the ozonide of *alpha*-isorubb

Alpha-isorubber and Its Degradation by Ozone

It has already been pointed out (p. 199) that the rubber hydrocarbon may be converted into rubber isomers by the elimination of hydrogen chloride from the rubber hydrochloride. Harries termed these transformation products isorubbers. The preparation of *alpha*-isorubber takes place according to Harries [203] as follows:—

1.2 to 1.4 kilograms of rubber are allowed to stand in 100 liters of benzene for several weeks. The resulting solution is then siphoned off and poured into an equal volume of alcohol to precipitate the rubber. One kilogram of this product is then suspended in about 20 liters of chloroform and a stream of gaseous hydrogen chloride is led into the cooled solution until it is saturated with the gas. When the resulting chloroform solution is poured into an equal volume of alcohol, the hydrochloride is formed as a white crumbly mass in a yield of 90 to 95 per cent of the theoretical amount. Small pieces of the hydrochloride together with seven times its weight of anhydrous pyridine are then placed in an autoclave provided with a stirrer, and the mixture while being efficiently stirred is heated in an oil bath at 125° to 145° C., for 24 hours. After this operation, the regenerated rubber is purified by washing it first with water and then boiling it for one hour under a reflux condenser with a 60 per cent solution of acetic acid. An after-treatment with water on the mill completes the purification process. The results of the analysis of *alpha*-isorubber agree very well with the formula $(C_5H_8)_x$.

Calcd. for $(C_5H_8)_x$: C, 88.15; H, 11.85; Cl, —
Found: C, 88.06; H, 11.30; Cl, 0.32

The *alpha*-isorubber cannot be obtained free from chlorine. The amount of chlorine which cannot be removed varies between 0.3 and 1 per cent. The yield, based on the crude rubber used, is at least 50 per cent. The properties of the *alpha*-isorubber are described by Harries [204] in the following manner: "The sheeted rubber can only be distinguished from good Para rubber by an expert. The toughness is not quite the same. Vulcanization tests have shown that the preparation readily combines with sulfur, but that the vulcanizate has only slight tensile strength (about like that of commercial alkali reclaim), so that in this form it possesses no practical worth." [205]

Various derivatives have been prepared from *alpha*-isorubber.[206] The hydrochloride is formed in the same way as the corresponding addition product of the normal rubber and does not differ from the latter in composition. The yields of the hydrochlorides are the same in both cases. Solid hydrohalides are also formed by the action of hydrogen bromide and of hydrogen iodide on *alpha*-isorubber. The tetrabromide is formed, as in the case of normal rubber. The tetrabromide of *alpha*-isorubber is, however, less stable than that of normal rubber and loses hydrobromic acid more readily on reprecipitation. Nitrous acid, after prolonged action on the *alpha*-isorubber, forms a product soluble in ethyl acetate; a shorter reaction time produces an insoluble yellow powder, the analysis of which differs considerably from that of "nitrosite C."

Calcd. for $C_{10}H_{15}N_3O_7$ (nitrosite C): C, 41.52; H, 5.20; N, 14.53
Found: C, 44.88; H, 5.50; N, 12.21

[202] *J. Chem. Soc.*, **97**, 1085 (1910).
[203] Harries, "Untersuchungen ....," p. 77, also *Ber.*, **46**, 733 (1913).
[204] Harries, "Untersuchungen . . . . . ," p. 78.
[205] Ger. Pat., 267,277, 267,993.
[206] O. Lichtenberg, *Ann.*, **406**, 227 (1914).

The structure possessed by *alpha*-isorubber differs from that of normal rubber by a partial displacement of the double bonds. This structural difference was first elucidated by ozonizing the *alpha*-isorubber and decomposing the ozonide. The decomposition curve for the ozonide of *alpha*-isorubber was essentially different from that for the ozonide of normal rubber. The products of decomposition contained ketones possessing eleven and fifteen carbon atoms. These ketones were not found among the decomposition products of the ozonide of crude rubber by Harries.

The ozonization was carried out according to the directions of Harries,[207] in a manner similar to that employed with rubber. The current of oxygen gas, which contained 8 to 10 per cent of ozone, was washed twice and was then led into the ethyl acetate or chloroform solution of the *alpha*-isorubber. The ozonide $(C_5H_8O_3)_x$ was reprecipitated three times from ethyl acetate with petroleum ether, and was then obtained as a white solid mass. The analysis was as follows:—

Calcd. for $(C_5H_8O_3)_x$: C, 51.70; H, 6.95;
Found: C, 51.67; H, 7.36

It is remarkable that in the decomposition of the ozonide with water, resins to the extent of 30 per cent are formed. The resulting acids are separated from the ketones and aldehydes by preparing the calcium salts with calcium carbonate. The ketone mixture after the separation was fractionated *in vacuo* at 0.3 mm. pressure. Part of the acids were distilled in the free state, and part after converting them to esters. In this way, Harries [208] succeeded in isolating a number of substances, which are listed in the following table:

1000 g. of isorubber yielded the theoretical amount of the ozonide, 1706 g.[209]

A lively evolution of gas takes place in the decomposition of the ozonide with water. The gases identified by Harries are given in the table under *a*.

	Per cent
a. Gaseous substances:	
1. Oxygen	0.068
2. Carbon dioxide	0.845
3. Carbon monoxide	0.183
4. Hydrocarbons	0.044
b. Hydrogen peroxide	1.04
c. Total aldehydes and ketones [210]	35.25
Fraction I—100° C.	
1. Levulinic aldehyde, about	9.0
2. Diacetylpropane, $C_7H_{12}O_2$	8.7
3. Methylcyclohexenone (Quantity not determined)	
Fraction II—150° C.	
4. Triketone, $C_{11}H_{18}O_3$	0.9
Fraction I and II also contained levulinic acid.	
Fraction III—250° C.	
5. Tetraketone, $C_{15}H_{24}O_4$	0.6
6. Oil, not identified, boiling point 220° to 260° C.	8.29
7. Resinous residue	9.3

[207] *Ber.*, **46**, 733 (1913).
[208] Harries. "Untersuchungen ....," p. 99; *Ann.*, **406**, 226 (1914).
[209] It is impossible to determine the number of double bonds in the isorubber from its oxygen content, since the quantity of oxozonide which is present is unknown. According to the analysis of the hydrochloride (O. Lichtenberg, *Ann.*, **406**, 227 [1914]) the double bonds of isorubber are not diminished in number by cyclization.
[210] Based on the quantity of rubber used.

d. Total acids	88.5
Fraction A	
1. Formic acid, about	18.3
Fraction B	
2. Levulinic acid, about	12.0
3. Succinic acid, about	1.5
Fraction C	
4. Hydrochelidonic acid	1.7
Fraction D	
5. Ester of methyl-carboxylic acid-cyclohexenone	1.7
Fraction E	
6. Other esters of higher-boiling non-identified acids	20.0
7. Resinous residue	6.4
8. Loss	26.9
e. Water-insoluble resin resulting from the decomposition of the ozonide by water	31.0

Aldehyde and Ketone Fraction. The aldehyde and ketone mixture is a light brown viscous liquid. The distillation of the mixture in high vacuum gives the substances listed under C. The appearance of levulinic acid in fraction I and II is noteworthy. This acid was probably present as the peroxide when the acids were separated by means of calcium carbonate and was later converted to levulinic acid.

The diacetylpropane of fraction I boils at 96.5° to 97° C. at a pressure of 10 mm. The elementary analysis gave the following values:

Calcd. for ($C_7H_{12}O_2$): C, 65.60; H, 9.40; Found: C, 65.54; H, 9.61

A value of 132 was obtained for the molecular weight, while the theoretical value for the above formula is 128. The molecular refraction was found to be 34.6; theoretically the value is 34.55. The substance was identified as diacetylpropane by preparing several derivatives of which the crystalline dioxime is especially suitable. In alkaline solution, the diacetylpropane melting at 87° C can easily be converted to methylcyclohexenone, which was also found in fraction II.

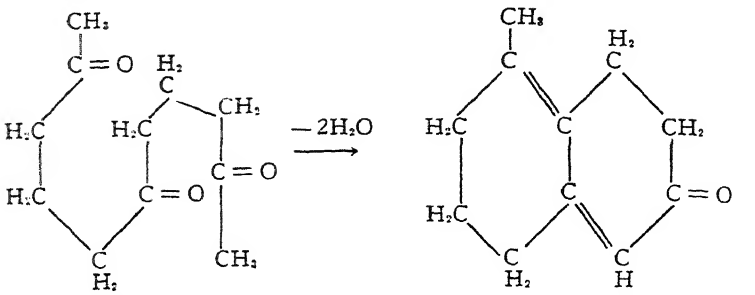
The principal constituent of fraction II, on the basis of an elementary analysis and a molecular weight determination, possesses the formula $C_{11}H_{18}O_3$ and is a triketone:

Calcd. for $C_{11}H_{18}O_3$: C, 66.7; H, 9.1
Found: C, 66.96; 67.32; 67.03; 66.69;
H, 9.33; 9.32; 9.34; 9.62

Molecular weight: Calculated, 196. Found, 196, 197. The triketone has a melting point of 93° to 94° C., and is difficultly soluble in ether and petroleum ether; more readily soluble in alcohol, benzene, and ethyl acetate, and very readily soluble in water.

According to its chemical behavior, the product can be classified as a triketone. A trioxime is formed with hydroxylamine; a trisemicarbazone with semicarbazide. Chemically the substance is similar to diacetylpropane, and Harries therefore regards it as a homologue of this substance. When heated with alkali the triketone undergoes a double inner condensation with a loss

of two molecules of water. Harries formulates this process as follows:



From fraction III Harries could isolate a tetraketone, having a melting point of 123° C. An elementary analysis and a molecular weight determination gave the following values:

Calcd. for $C_{15}H_{24}O_4$: C, 67.10; H, 8.90
Found: C, 66.66; H, 8.86
Molecular weight: calculated, 268. Found, 269.

The tetraketone possesses almost the same properties and solubilities as the triketone. The tetraketone is more difficultly soluble in the solvents mentioned in connection with the triketone. With hydroxylamine it forms a tetroxime which has a melting point (with frothing) when recrystallized from acetic acid of 112° to 113° C. The analytical values of the tetroxime correspond to the formula $C_{15}H_{28}O_4N_4$. A lack of material prevented further investigation of this substance.

Acid Fraction. If the acids which have been liberated from the calcium salts are directly distilled, they are decomposed for the most part. To avoid this, Harries converted them into the methyl esters and could separate them in this way.

The relatively large amount of formic acid in fraction A is noteworthy since this amount could not be entirely formed from a terminal group at the end of the chain, which would have to be the case if the open-chain formula for rubber is assumed.

Fraction B contains nearly pure methyl ester of levulinic acid, the hydrazone of which melts at 105° to 106° C. At times small quantities of succinic acid were found in this fraction.

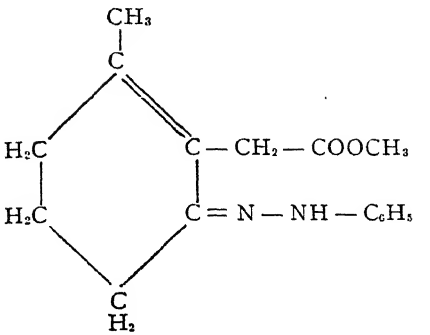
Fraction C melted at 60° C. and according to an elementary analysis was the methyl ester of hydrochelidonic acid.

Calcd. for $C_9H_{14}O_5$: C, 53.5; H, 6.9
Found: C, 53.32; H, 6.85.

A product prepared synthetically for purposes of comparison was identical with the above.

An unsaturated ester of a cyclic ketonic acid was isolated from Fraction D, by means of phenylhydrazine. This ester was probably formed as the result of an inner condensation of an ester of a diketonic acid. From the results of the analysis, the compound is apparently the phenylhydrazone of the methyl ester of 1-methyl-2-methanecarboxylic acid-2-cyclohexenone.

Calcd. for $C_{16}H_{20}O_2N_2$: C, 70.60; H, 7.30; N, 10.30
Found: C, 70.81; H, 7.20; N, 10.68



From the higher boiling fraction no definite crystalline products could be obtained.

Beta-Isorubber

With hydrochloric acid, a hydrochloride can also be prepared from *alpha*-isorubber. If hydrochloric acid is eliminated from this product by means of pyridine under pressure, a 44 per cent yield of the *beta*-isorubber is obtained as a violet-black elastic product.[211] This isorubber is more readily soluble than normal rubber in the usual solvents for rubber and can only be precipitated with difficulty from a benzene solution by means of alcohol. The elementary analysis gave the following values.

Calcd. for $(C_5H_8)_x$: C, 88.15; H, 11.85; Cl,
Found: C, 88.31; H, 11.82; Cl, 0.03.

If a solution of this substance in ethyl acetate is treated with a rapid stream of unwashed ozone, a quantitative yield of the yellow oily ozonide is produced.

Calcd. for $(C_5H_8O_3)_x$: C, 51.70; H, 7.01
Found: C, 49.75; H, 6.95

Harries [212] investigated the decomposition products of this ozonide in a manner analogous to that described under *alpha*-isorubber. It is not worth while to consider the results further, since they led to no new views on the constitution of rubber.

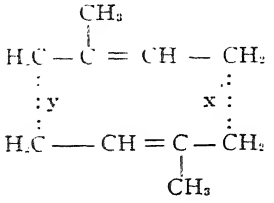
The hydrochloride, bromide, and nitrosite of *beta*-isorubber were prepared by Harries. The hydrochloride is a brown powder which begins to decompose at 140° C. and is completely decomposed at 185° C. The analytical results recorded by Harries do not agree very well with the formula $(C_5H_8HCl)_x$. The analyses of the bromide and nitrosite derivatives indicate that they are not definite substances. This is not surprising, since the crude rubber itself is a mixture which has become more complex by repeatedly forming the hydrochloride and regenerating the original rubber.

Theoretical Deductions from the Ozone Degradation

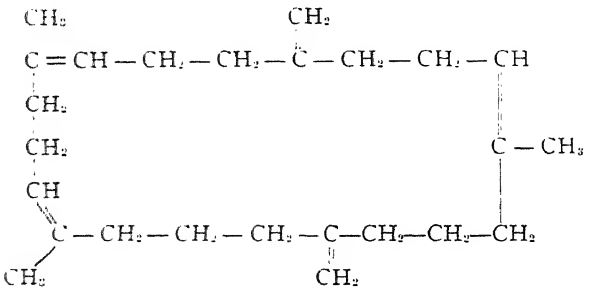
From the investigations on the degradation of *alpha*-isorubber, Harries was able to draw conclusions of importance in connection with the chemistry of the rubber hydrocarbon. Previously the chemical behavior of rubber could very well be explained by the assumption of the 1,5-dimethylcyclooctadiene formula. The formation of levulinic acid and levulinic aldehyde can readily be explained by an eight-membered ring formula. If displace-

[211] Harries, "Untersuchungen ....," p. 23. [212] "Untersuchungen ....," p. 100.

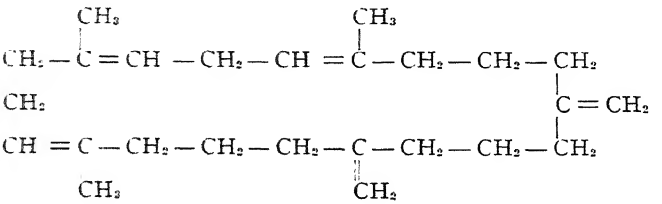
ment of the double bonds in the eight-membered ring formula is assumed, then the formation of diacetylpropane can also be explained. The decomposition products containing 11 and 15 carbon atoms, the tri- and tetraketones respectively, can no longer be explained on the basis of this formula. To justify the presence of the ketones, Harries proposed an extended ring formula:



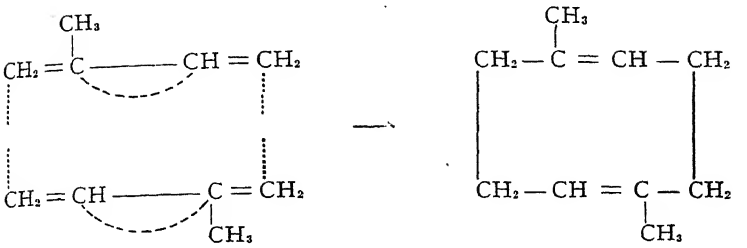
The dotted lines represent additional isoprene groups, the number of which is not fixed. In 1914, Harries considered a ring formula consisting of four or five isoprene groups as the most probable, since the formation of all the decomposition products could be explained by such a formula. The *alpha*-isorubber might possess the following formula, if hydrogen chloride is split off by the removal of a hydrogen atom other than the hydrogen atom added:



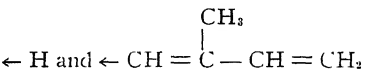
This substance would yield the following decomposition products: 1 mol of levulinic aldehyde (or levulinic acid), 1 mol of triketone and 1 mol of hydrochelidonic acid, 2 mols of formic acid or formaldehyde. The following formula for *alpha*-isorubber would explain the formation of the tetraketone:



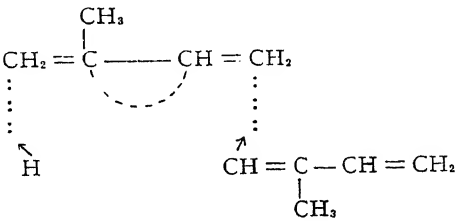
The formation of cyclic hydrocarbons which are built up symmetrically from isoprene groups is easily explained if this conjugated system reacts at the terminal groups.



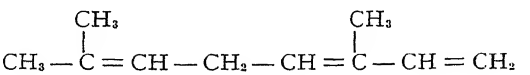
The carbon linking in the 1,4 position is then obtained. The original double bonds disappear and the inactive double bonds of the isoprene molecules (according to Thiele) become actual double bonds in the new ring system. In the simplest case, dimethylcyclo-octadiene would result. A greater number of isoprene groups could also be combined in a cyclic manner, according to this scheme. Only levulinic aldehyde or levulinic acid would be formed by the ozone degradation of such ring systems, but from the decomposition it would be impossible to determine the number of isoprene groups united in a closed-chain in the molecule. It is also possible, however, that isoprene polymerizes in other ways, e.g., to produce an open-chain polymer. It could be assumed that an isoprene molecule adds the components of a second molecule,



in the 1,4-position according to the following scheme:



An open-chain dimer with three double bonds would then be formed.



Such a compound (an aliphatic terpene) on ozonization would yield entirely different decomposition products, namely, from left to right: acetone, malonic di-aldehyde (which is always destroyed by ozone, according to Harries), methylglyoxal and formaldehyde. If additional isoprene groups are attached in the same manner to the conjugated system at the 1,4-position to produce a longer chain, then aliphatic hydrocarbons would always result,[213] which on decomposition with ozone should form, among other products, acetone and

[213] Derivatives of such "open-chain" terpenes with 2 to 4 isoprene members occur in nature and have recently been investigated by Ruzicka. The alcohol phytol of chlorophyll (C_{20}....) and the carotinoids are genetically related to such terpenes through hydrogenation or dehydrogenation.

methylglyoxal (or succinic acid). Harries expressly sought to obtain these substances by conducting ozonization experiments with one-half kilogram of rubber, but never found them, despite the very good methods available for their detection. For this reason, he does not incline to the open-chain type rubber formula which was first proposed by Weber [214] and which has recently assumed greater importance through the work of Staudinger and Fritschi.

The Hydrogenation of Rubber

Significance of Hydrogenation in the Determination of the Constitution of Rubber

According to the results obtained in studying the addition to rubber of the halogens, halogen acids, and ozone, the hydrogenation of rubber should result in the addition of two hydrogen atoms for each C_5H_8 group in the molecule. The preparation of hydrorubber was important because it should have furnished important evidence regarding the size of the rubber molecule. If Harries were correct in his assumption that rubber consists of a relatively small cyclic parent molecule of four or five isoprene groups united reversibly by means of residual valences to form the complex "aggregate" of natural rubber, then it was to be expected that after saturating the double bond, the tendency toward aggregation would disappear, and a molecular weight determination could be made. Again, distillation of a saturated hydrocarbon of high molecular weight in high vacuum promised far better results than the distillation of an unsaturated hydrocarbon. Harries, in his book "Untersuchungen über die natürlichen und künstlichen Kautschukarten," expresses himself as follows: "The hydrorubber could probably be distilled in high vacuum, and in this way its constitution could be determined."

The importance of this reaction was early recognized, and many experiments on the hydrogenation of rubber were performed. Berthelot [215] heated rubber, as well as coal and many other organic substances, with concentrated hydriodic acid in a bomb tube, and obtained a mixture of high-boiling paraffins.

Catalytic Hydrogenation According to the Method of Staudinger and Fritschi

The rubber molecule behaves singularly in its great resistance toward mild hydrogenation with platinum black, according to the method of Fokin-Willstätter. Neither Harries [216] nor Hinrichsen and Kempf [217] succeeded in bringing about saturation of the rubber with hydrogen according to this method. The catalytic hydrogenation of rubber was accomplished by Staudinger and Fritschi, and simultaneously by Pummerer and Burkard, in the year 1922.[218] Staudinger and Fritschi [219] accomplished the addition of hydrogen to rubber by using a high temperature and a hydrogen pressure of about 100 atmospheres. They placed the rubber, previously melted and mixed with platinum black, in a rotating autoclave, without the addition of solvent, and attained complete hydrogenation in 10 hours at 270° C. and a

[214] *Ber.*, **35**, 3256 (1902).
[215] *Bull. soc. chim.*, (2), **11**, 33 (1869).
[216] Harries, "Untersuchungen ....," p. 48.
[217] *Ber.*, **45**, 2106 (1912).
[218] *Cf.* Harries, *Ber.*, **56**, 1050 (1922).
[219] *Helv. Chim. Acta*, **5**, 785 (1922); see also Staudinger, Brunner, and Geiger, *ibid.*, **13**, 1368 (1930).

pressure of 92 atmospheres. The rubber, which was originally brown, had become light in color and was stable toward bromine. The elastic properties of the natural rubber were entirely absent in Staudinger's hydrorubber. The product was soluble in benzene, chloroform, and ether, and insoluble in alcohol and acetone. The elementary analysis gave the following values:

Calcd. for $(C_5H_{10})_x$: C, 85.71; H, 14.38;
Found: C, 85.75; 85.69; 85.97. H, 14.58; 14.45; 13.97.

At that time, its molecular weight in benzene was too high to be determined. For the further investigation of the nature of the hydrorubber, Staudinger and Fritschi subjected the substance to distillation at a pressure of one millimeter. The hydrorubber was decomposed in this operation into a series of unsaturated hydrocarbon compounds. The temperature necessary to accomplish this was about 50° C. higher than is necessary with normal rubber, and was between 350° and 390° C. The fore fraction (I), which was collected in a receiver cooled to — 80° C., amounted to 6.7 per cent; the residue in the flask was equal to 0.6 per cent of the rubber. By fractional distillation at four millimeters pressure, the crude distillate was separated into six fractions (*See* Table 4).

TABLE 4.—*High Vacuum Distillation of Hydrorubber by Staudinger and Fritschi.*

Fraction	B.p. °C.	Yield in per cent	Mol. V
I	Collected in a receiver cooled to -80	6.7	—
II	55—75	10.1	—
III	75—150	6.1	—
IV	150—220	16.9	210
V	220—270	17.6	—
VI	270—315	22.3	600
VII	315—320	24.3	700
Residue	—	0.67	—

The individual fractions contained unsaturated hydrocarbons. The highest-boiling portion was found in fraction VII. The boiling point of this fraction on repeated distillation was found to be 268° to 275° C. at 0.014 millimeters pressure. According to the analysis and the molecular weight determination, the product is a long-chain olefin, $C_{50}H_{100}$.

Calcd. for $(C_5H_{10})_x$: C, 85.71; H, 14.28
Found: C, 86.08; 86.22; H, 14.13; 14.02

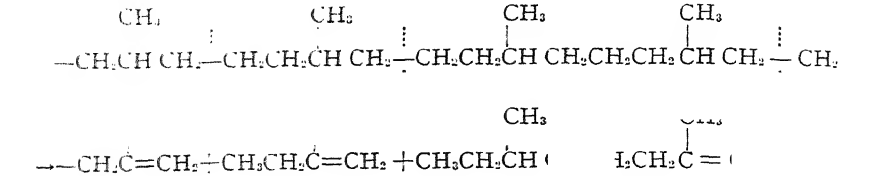
The molecular weight was determined in benzene.

Calcd. for $C_{50}H_{100}$; mol. wt., 700. Found: 698, 693, 684.

Recently, Staudinger [220] has given the molecular weight of the largest member resulting from the decomposition as $C_{40}H_{80}$. The product reacts with bromine, and titration with this reagent points to one double bond for the complex, $C_{40}H_{80}$. The remaining fractions contain unsaturated hydrocarbons of lower molecular weight with 45, 30 and 15 carbon atoms. In the lowest-boiling portion there is present a pentene, methylethylethylene. The pyro-

[220] *Kautschuk*, **1**, Sept. 1 (1925). Recently $C_{65}H_{130}$, *Kautschuk*, **5**, 96 (1929).

genetic decomposition of hydrorubber is formulated as follows by Staudinger and Fritschi:



From the size of the decomposition products resulting from the distillation of hydrorubber, they concluded that the rubber molecule is composed of at least 16 isoprene groups (corresponding to 2 times $C_{40}H_{80}$) and probably contains hundreds of isoprene groups linked together to form a long open-chain structure.

Catalytic Hydrogenation According to the Method of Pummerer, Burkard and Koch

With sensitive natural products, such as the terpenes and rubber, it is necessary to carry out reactions which serve the purpose of determining the constitution, under the mildest conditions available. Conclusions regarding the constitution of the original rubber molecule are no longer possible after the rubber has been treated according to the drastic hydrogenation method of Staudinger at 270° C. Staudinger himself found that in the absence of hydrogen, rubber is changed to a resinous, benzene-insoluble substance at 270° C. According to Staudinger, this latter reaction is almost entirely absent when the hydrogenation is systematically controlled. His latest results on the comparison of the refraction of hydrorubbers prepared by various processes show that his hydrogenation method at 270° C. does not give a satisfactory hydrorubber.[221] For the determination of the constitution, it is essential that the hydrogenation be conducted at a temperature at which the rubber molecule suffers no damage. Simultaneously with Staudinger's work, Pummerer and Burkard [222] showed that the hydrogenation of rubber in very dilute solutions (0.2 to 0.6 per cent in hexahydrotoluene) can be accomplished at 80° C. with platinum black and hydrogen. The reaction proceeds more slowly in the cold. The hydrogenation was further improved by Pummerer and Koch [223] by using a large excess of platinum black, and rubber which was very carefully purified by fractional precipitation. Extreme purity and large dilution of the rubber are essential for success.[224]

The platinum black was added in small portions. After each addition, the reaction was allowed to cease before the next portion was added. The volume of hydrogen consumed was read from measuring cylinders. A 0.9 per cent solution of purified rubber, in hexahydrotoluene, was used for the hydro-

[221] E. Geiger, Dissertation, Zurich; also compare *Helv. Chim. Acta*, **7**, 844 (1924), Footnote 2. In the dissertation of Geiger is described a combined hydrogenation process in which the reaction is carried out in very dilute solution, at a temperature of 130° to 140° C., at 100 atmospheres pressure with nickel as a catalyst. The catalyst consists of nickel hydroxide, $Ni(OH)_2$, deposited on a carrier (25 per cent $Ni(OH)_2$ by weight). One part of catalyst to one part of rubber is used. Cobalt also seems to give satisfactory results.

[222] *Ber.*, **55**, 3458 (1922).

[223] *Ann.*, **438**, 303 (1924).

[224] *Cf.* also the German patent application of Oct. 5, 1923, by Siemens & Halske A. G. (n. 560 49 *IV*/39b, 1), which originated with Harries [*Ber.*, **56**, 1051 (1923)] and in which a catalytic process is described, permitting hydrogenation of dead-milled rubber in an autoclave at ordinary temperature. Harries, in another place, attacks scientific conclusions drawn from the results of hydrogenation conducted at 270° C.

genation. The purified rubber used was obtained by repeated fractional precipitation and was completely soluble in ether and hexahydrotoluene.

The volume of hydrogen consumed during hydrogenation was not a measure of the amount absorbed by the rubber, since an excess of platinum black was used (nearly 10 parts of platinum black, to one part of rubber). The hydrorubber, when freed from the platinum black, was a transparent, white, tough mass, and possessed a tendency toward crystallization.[225] The sides of the flask were covered with hydrorubber. This hydrorubber, when free from the solvent, exhibited individual dendritic forms and tabular elastic crystals which unfortunately could not be isolated. The hydrorubber did not react with bromine or alkaline permanganate solution.

Analysis, Calcd. for $(C_5H_{10})_x$: C, 85.63; H, 14.37
Found: C, 85.78; H, 13.95

Distillation in high vacuum yielded further information about the substance. At 354° C. and 1.5 mm. hydrogen pressure (the capillary tube was supplied with hydrogen), the hydrorubber distilled with very little indication of decomposition.[226] The distillate was light yellow in color and possessed an odor, due to decomposition products, similar to that of limonene. The distillate was purified by dissolving it in boiling acetone, from which an odorless and colorless oily substance deposited on cooling. This substance was completely stable toward bromine and permanganate. The elementary analysis and the determination of the average molecular weight in camphor, by Rast's method, gave the following values:

Calcd. for $(C_5H_{10})_x$: C, 85.63; H, 14.37
Calcd. for $C_{50}H_{102}$: C, 85.38; H, 14.62
Found: C, 85.40; H, 14.52
Calcd. for $C_{50}H_{102}$: mol. wt., 702; Found: 714

It is impossible to distinguish between the compound of formula $C_{50}H_{100}$ (monocyclic) and that of the formula $C_{50}H_{102}$. It is noteworthy that the hydrorubber prepared with the aid of heat corresponds closely to the formula $(C_5H_{10})_x$, while the hydrorubber prepared in the cold contains 0.3 to 0.4 per cent less hydrogen. The above distillate obtained from hydrorubber also shows the higher hydrogen values corresponding to the formula $(C_5H_{10})_x$. Either partial cyclization accompanies the hydrogenation in the cold (*see* page 228) or else the hydrorubber contains ring systems which, on heating, are split off as unsaturated hydrocarbons from the principal chain, which remains saturated.

The distillate is a very viscous, colorless mass, which is soluble in hot acetone and in ether, chloroform, and hydrocarbons, in the cold. The substance is, without doubt, a saturated hydrocarbon. The hydrogenation of rubber in the cold was recently reinvestigated by Pummerer and Hilde Nielsen.[227] The results of Pummerer and Koch were essentially confirmed.

[225] Crystallized rubber (*see* p. 168) as well as this hydrorubber was obtained from thoroughly masticated sheet rubber. No tendency toward crystallization was observed with hydrorubber prepared from rubber obtained from ammonia-preserved latex.

[226] See *Helv. Chim. Acta*, **13**, 1355 (1930); *Rubber Chem. Tech.*, **5**, 131 (1932).

[227] *Ber.*, **60**, 2167 (1927) and dissertation of H. Nielsen, Erlangen, **1926**. The question of the susceptibility of hydrorubber toward air was reinvestigated. Pummerer and Burkard maintained that the susceptibility was due to the presence of platinum. This statement was confirmed by Harries, *Ber.*, **56**, 1050 (1923), but was questioned by Staudinger, *Ber.*, **57**, 1207 (1923). It is certain that hydrorubber which is completely free from platinum is not sensitive to air at room temperature. However, the crude product of the hydrogenation in the cold, containing colloidal platinum in small quantities, is affected by the oxygen of the air, according to recent experience of H. Nielsen. A dehydrogenation of rubber does not take place, but more probably absorption of oxygen. Platinum recovered from the hydrogenation is rich in hydrogen. Perhaps local autoxidations take place, which also involve the hydrorubber at elevated temperatures.

However, on distillation under a pressure of 1 mm. (MacLeod-manometer) a distillate was obtained having an average molecular weight of 1250 (acetone-soluble portion) to 1560 (difficultly acetone-soluble portion). Similar and even lower values were observed with crude undistilled hydrorubber and hydrocyclorubber, which was boiled only with acetone to remove oxygen-containing impurities. The hydrocarbon $C_{50}H_{102}$ might well be a decomposition product of hydrorubber, since the latter does not begin to distil until a temperature of about 380° C. is reached. If the hydrocarbon $C_{50}H_{102}$ were originally present, it should begin to distil at a lower temperature. Perhydrolycopin, which has recently been prepared by P. Karrer and R. Widmer,[225] and which, like hydrorubber, is probably built up according to the isopentane system, has the formula $C_{40}H_{82}$ and boils at 238° to 240° C. at 0.03 mm. It is even possible that hydrocarbons having a molecular weight of 12,000 to 15,000 could constitute the more volatile portions of hydrorubber. Since the distillation never proceeds entirely without decomposition, this assumption has not been confirmed.

Staudinger and A. Peter [229] recognized the usefulness of the hydrogenation method in dilute solution, but still used high pressures (60 atmospheres). This condition is essential, since the velocity of reaction is thereby increased while the danger of side reactions (cyclization) and incomplete reaction is liminished. While Staudinger and Fritschi originally reported that the molecular weight of the hydrorubber prepared according to their process at 270° C. was too high to be determined, Staudinger [230] in 1926 reported values from 3,000 to 10,000, and more recently, 3,000 to 5,000,[231] all values being measured in benzene. In determining the later values, the investigators were probably working with hydrorubber prepared in dilute solution by the milder method of hydrogenation. The fact that platinum black, during hydrogenation, activated not only hydrogen but also the double bond is evident from cyclization phenomena (see "Abnormal Hydrogenation," p. 229). Polymerization reactions may, therefore, also accompany hydrogenation.[232] Molecular weight determinations of hydrorubber in benzene give values from 2,000 to 4,000 higher than those in camphor. With hydrocarbons of such high molecular weight, association may easily be the cause of the difference. Karrer and Rosmer, for example, obtained a value of 845 for the molecular weight of perhydrolycopin in bromoform, and a value of 525 (or 565) in benzene. In this case we are dealing with a smaller molecule, but the value for the molecular weight in benzene is obviously the correct one.

Staudinger explains the results of the hydrogenation otherwise. He does not attempt to deduce the molecular weight of rubber from a molecular weight of 3,000 to 5,000 for hydrorubber, but believes that degradation occurs during hydrogenation.[233] The drastic method of hydrogenation at 270° C. may possibly involve degradation, but it is improbable that degradation takes place when the milder method of hydrogenation is employed. Analogous instances do not exist in which aliphatic hydrocarbons are decomposed during mild hydrogenation. The possibility of degradation, as a side reaction of hydrogenation, can not be excluded any more than the possibility of synthesis. However, it is probable according to all present knowledge, that in the conversion of rubber to hydrorubber no change in the structure of the carbon chain takes place.

[225] *Helv. Chim. Acta*, **11**, 751 (1928).
[229] *Ber.*, **57**, 1207 (1924).
[230] *Ber.*, **59**, 3040 (1926).
[231] *Ber.*, **61**, 2589 (1928).
[232] R. Kuhn, working with carotinoids, even observed polymerization reactions when using aluminum amalgam.
[233] This conception is in accord with the hypothesis that the rubber molecule can dissociate, mentioned on page 188.

In a series of articles Staudinger and his co-workers* [H. Staudinger and J. Senior, *Helv. Chim. Acta*, **13**, 1321 (1930); H. Staudinger, *ibid.*, **13**, 1324 (1930); H. Staudinger, E. Geiger, E. Huber, W. Schaal and A. Schwalbach, *ibid.*, **13**, 1334 (1930); H. Staudinger and R. Nodzu, *ibid.*, **13**, 1350 (1930); H. Staudinger and W. Schaal, *ibid.*, **13**, 1355 (1930); H. Staudinger and W. Feisst, *ibid.*, **13**, 1361 (1930); H. Staudinger, M. Brunner and E. Geiger, *ibid.*, **13**, 1368 (1930); see also *Rubber Chem. Tech.*, **4**, 365, 524, 532, 534 (1931); **5**, 131, 136, 141 (1932)] have greatly extended our knowledge on hydrorubber. Rubber was hydrogenated with phosphorus and hydriodic acid at 240° to 280° C. Partial cracking and cyclization of the rubber molecule accompanied hydrogenation, and completely saturated hydrocarbons were formed.

If rubber is heated without a solvent, and at the same time very rapidly hydrogenated, hemi-colloidal hydrorubber results. The hydrogenation rate with various catalysts was studied at 275° to 280° C. under 100 atmospheres pressure. Ni, Co, Pt, Fe, and Cu catalysts were used. Molecular weight determinations by cryoscopic methods and viscosity measurements agreed well and gave values from 1,600 to 10,000.

A hydrorubber with a molecular weight of 14,000, when fractionally precipitated from ether solutions by alcohol gave fractions ranging in molecular weight from 5,000 to 21,000.

Hydrorubbers of high molecular weights (31,000) were obtained by hydrogenating sol- and gel-rubber in methylcyclohexane with platinum as catalyst.

The hydrogenation of methylrubber at high temperatures was also studied.

Abnormal Hydrogenation

Pummerer and Koch,[234] in 1924, pointed out that rubber is hydrogenated in an abnormal way with platinum black and hydrogen, resulting in the formation of a saturated hydrocarbon (obviously accompanied by partial cyclization) which has absorbed only one-half the expected amount of hydrogen. Such partially hydrogenated, partially cyclic products are frequently formed.[235] Finally, some cases occur in which only the double bonds disappear, and no hydrogenation takes place by the action of platinum black and hydrogen. Analogous results have not been obtained by using platinum black and nitrogen. It has not been definitely shown that the removal of the double bonds is always due to cyclization, as Staudinger assumes, and that the reaction is therefore mono-molecular. Polymerization reactions such as di- or poly-molecular reactions are also probable. Pummerer and Nielsen observed values of 2000 for the average molecular weight of a sample of rubber which was prepared according to the above process, with platinum and hydrogen, and was almost completely cyclicized.[236]

The conditions under which abnormal and normal hydrogenation take place, and under which cyclization results, cannot be determined from our present knowledge, and probably depend upon the catalyst, the sample of rubber, its previous history, and its impurities. All of the methods for the hydrogenation of rubber, disregarding the method involving the severe reaction at 270° C., are unreliable and leave much to be desired. Hydrorubber is a highly viscous paraffin hydrocarbon, and as such may perhaps have commercial possibilities. The same may be said of many hydrocyclorubbers which melt at low temperatures and which are similar to Bakelite in that they are not attacked by chemical reagents.

Homologs of Hydrorubber

Staudinger and Widmer[237] have prepared homologs of hydrorubber by treating rubber hydrobromide with zinc dialkyl compounds. Methyl-ethyl

* Translator's Note.

[234] *Ann.*, **438**, 310 (1924).

[235] Pummerer and Nielsen, *Ber.*, **60**, 2171 (1927).

[236] Nielsen, Dissertation, p. 33.

[237] *Helv. Chim. Acta*, **7**, 842 (1924).

hydrorubber cannot be prepared readily and in an analytically pure state, since partial liberation of the halogen acid also takes place and probably condensation also occurs. The alkyl hydrorubbers give very viscous colloidal solutions and, as paraffin hydrocarbons, are stable toward nitric acid and permanganate. They do not lower the freezing point of benzene. Replacement of zinc alkyl compounds by alkyl magnesium halides gives a different result, and produces unsaturated hydrocarbons. An experimental effort toward converting rubber hydro-iodide into hydrorubber by means of the magnesium compound gave negative results.

Trimethylamine reacts with rubber hydrohalides in the same manner as does the Grignard compound, with the formation of unsaturated derivatives (regeneration of rubber or is rubber). On the other hand, Staudinger succeeded in preparing water-soluble saturated phosphonium salts from rubber hydrobromide, by means of trialkylphosphine. These salts give highly colloidal water solutions such as are formed with soaps and many dyestuffs. The molecular weight can in no case be deduced from the colloidal nature, since the colloidal properties of substances are strongly influenced by their constitution (compare the meta derivatives of the benzidine series in the case of the substantive azo dyes).

Molecular Size and Constitution of Rubber

General

The determination of the constitution of the colloidal rubber hydrocarbon is primarily of theoretical interest. The study of the naturally occurring substances of high molecular weight, which play such an important part in animal and plant life, has in the last decade become a favored field of exploration in organic chemistry, colloid chemistry, and x-ray chemistry. Although rubber is a complex substance, it is constructed according to a relatively simple plan, and the constitutional relations are less involved than in the case of cellulose, starch, or proteins. The investigation of rubber may answer such fundamental questions as to whether the size, the form, or the unsaturated character of a molecule (residual valences and van der Waal's forces), determine the colloidal properties of a substance. The possible causes of the colloidal properties of a molecule are of the greatest interest in determining its constitution, because they are little understood, and few correlated experiments are recorded concerning them. A sharp distinction between the structural chemistry and the colloidal chemistry of rubber is not yet possible, and the investigation of the constitution of rubber should aim to explain the structure of the colloid chemical micelles.

Organic substances which form lyophilic colloid solutions are divided into two main groups: the true colloids and the association colloids. Typical true colloids (also called eucolloids by Staudinger) include substances such as proteins, which have an established molecular weight of about 16,000 (hemoglobin) and which give colloidal solutions in all solvents suitable for the investigations. With hemoglobin, there is a stoichiometrical indication of the molecular size, since each molecule having a molecular weight of 16,000 contains one atom of iron (which certainly belongs to the molecule and is not an impurity). With other proteins which do not contain such a readily determinable stoichiometrical equivalent, the question of molecular size is

more difficult to answer. If in the decomposition of a protein a certain amino acid is produced to the extent of 1 per cent, this value may be accepted as an equivalent, if it is certain that it does not result from an impurity. It is always difficult to avoid the formation of amino acids from impurities when dealing with non-crystalline substances which may be mixtures.

The stoichiometrical molecular weight determination from the equivalent fails with non-crystalline substances. There remain then only the physical methods, such as the measurement of osmotic pressure, diffusion velocity, dialysis, and the use of the ultra-centrifuge. The ultra-centrifuge, devised by The Svedberg,[238] has given especially valuable results in his hands. He has found, in hemoglobin solutions, particles having a molecular weight of 33,000 (thus containing two iron atoms), of 66,000 (the main part), and of 99,000. Egg albumin also gave a value of 33,000. In spite of the simple numerical ratio (1:2:3) by which the hemoglobin particles are related to one another and to the value 16,000, he regards them as molecules and not as micelles.

H. R. Kruyt[239] who spent years in the investigation of lyophilic colloid solutions, assumes that in agar and gelatin solutions, there exist micelles which in turn are built up of bundles of molecules and solvent.

In the determination of the molecular weight (or better still, "mean particle size") by physical methods, values are frequently obtained which are characteristic for the substance in the particular solvent. A determined particle size is dependent not only upon the actual particle size, but also upon the formation of micelles from the molecules. The molecules combine with each other or with the solvent to form a colloid chemical unit, the micelle. The number of particles decreases with micelle formation (association). The question of micelle formation, and the average number of molecules which form a micelle, becomes important in dealing with the second group of colloids which, in contrast to the eucolloids, are best designated as "association colloids." To this class belong the soaps and the so-called substantive azo dyes of the benzidine series. In these substances there are present relatively small molecules containing 16 to 40 carbon atoms, which could be called "unit" or "parent" molecules. In certain solvents, for example water, micelles are formed by association of many of these unit molecules and ions. In other solvents, molecular dispersion takes place, and the unit molecule can then be identified by osmotic methods. It would therefore be futile to attempt to determine the molecular size of fatty acids by means of cryoscopic measurements in water. Experiments must be undertaken in many solvents (excluding of course those which decompose the substance) and the smallest value found is then taken as the size of the unit molecule.

Determination of the Average Particle Size of Rubber in Solution

At the present time there is a lively debate as to whether rubber and the polysaccharides are to be considered true colloids (eucolloids) or association colloids. This has not been a purely academic discussion, for the opposing views serve as working hypotheses, which have led to many important results on both sides of the question. It has therefore been a fruitful battle of opinion, as should always be the case in natural science.

[238] The Svedberg and B. Sjörgren, *J. Am. Chem. Soc.*, **50**, 3318 (1928).

[239] *Kolloidchem. Beihefte*, **28**, 1 (1928).

By Cryoscopic Methods

The view that rubber is an association colloid was first proposed by C. Harries, who sought to explain upon this basis the variations in solubility and plasticity which occur according to the method of preparation of the rubber. (*Cf.* his "Modifications" on p. 163.) He could not conclusively state the size of the rubber molecule.

Recently, Pummerer and his co-workers extended the cryoscopic investigation of rubber to various solvents, seeking to prove experimentally the hypothesis of the relatively small unit molecule. Jointly with H. Nielsen and W. Gündel, Pummerer was able to show that very distinct depressions of the freezing points were obtained with the cryoscopic method, when rubber was dissolved in camphor, benzylidine-camphor, or menthol. In the case of camphor, an average molecular weight of 1200 to 1600 was indicated, when the proportion of rubber to camphor varied from 1 : 4 to 1 : 20, and when the determinations were carried out according to Rast's method (melting-point determination). Approximately the same particle size was also found for rubber when tested in menthol (2 per cent solution of rubber) in a Beckmann apparatus. With lower concentrations, unreliable values were obtained. Since a molecule composed of sixteen isoprene groups has a molecular weight of 1,088, and one composed of twenty-four isoprene groups has a molecular weight of 1,536, it follows that rubber in camphor has an average molecular weight which corresponds to from sixteen to twenty-four isoprene groups. Gutta-percha, under the same conditions, showed a measurable molecular weight of about 2,100 for the unit molecule.[240] Another important observation was that the solution of rubber in menthol is different from the ordinary solution of rubber (for example, in benzene) in that *no swelling* takes place. Sol-rubber also swells only slightly in benzene and dissolves very rapidly.

Pummerer and Nielsen substantiated the measurements carried out on rubber itself by other experiments with hydrorubber, cyclorubber (*see* p. 228), and hydrocyclo-rubber, which gave values of similar magnitude.

Among cryoscopic measurements on other types of rubber may be mentioned the subsequent work of Bruni and Geiger on the highly colloidal rubber nitrone described by Pummerer and Gündel.[241] This substance gives molecular weight values of 1,200 to 1,400 in benzene and in nitrobenzene, the most commonly used cryoscopic solvents. Eight isoprene groups plus eight nitrosobenzene molecules minus sixteen hydrogen atoms are equivalent to a molecular weight of 1,384. As in the case of menthol, these cryoscopic measurements cannot be made immediately after the disappearance of the solid substance. One to two hours (five to twelve hours with menthol) elapse before a constant final value is reached. This time interval is required to bring about the molecular dispersion of the micelles in the solvent [*see* Staudinger and Joseph, *Ber.*, **63**, 2888, 2900 (1930); *Rubber Chem. Tech.*, **4**, 191 (1931)].

In this connection it may be mentioned that Harries obtained molecular weight values of 1,100 to 1,700 for the primary rubber nitrosite A in methyl acetate. Because of the ease with which this nitrosite is decomposed, no special importance is attached to these measurements.

Staudinger[242] raised a series of objections to the molecular weight deter-

[240] H. Brunswig, "Über Guttapercha," Thesis, Erlangen. See also H. Miedel, *Kautschuk*, **3**, 232 (1927), who reports a value of about 1200 to 1600.

[241] See p. 205 and *Ber.*, **61**, 1591 (1928).

[242] With M. Asano, H. F. Bondy, and R. Signer, *Ber.*, **61**, 2575 (1928).

minations of rubber in camphor. In the first place, rubber is decomposed at 180° C. and can catalytically decompose the camphor. Furthermore, an impurity containing oxygen, which can be separated in high vacuum, is the cause of the low values for the molecular weight of rubber. These objections and others have all been refuted.[243]

A more fundamental objection proposed by K. H. Meyer and H. Mark[244] needs more serious consideration. They questioned the use of the cryoscopic method with such colloidal or semi-colloidal systems as have been discussed above. They emphasized the definite retardation of the velocity of crystallization of the solvent, and the marked effect of low molecular weight impurities which are difficult to remove in the case of a natural product such as rubber. On the basis of the crystallite lengths which were measured in stretched rubber (*see* p. 169), they assumed as probable a principal valence chain consisting of 75 to 150 isoprene groups (average molecular weight of about 5000). A great number of chains, adjacent to each other and bound together by lattice forces, produce the crystallite of the stretched rubber, which assumes the form of a long, narrow tube. From these molecular aggregates, micelles are formed in solution, after swelling and partial disintegration has occurred.

The objection concerning impurities which has been raised by the above-mentioned authors and others, in the field of rubber, has also been mentioned in the case of carbohydrates and proteins. Objections concerning this source of error do not seem to be justified, at least in the case of rubber. Apparent molecular weights of 5,000 can be influenced by impurities; but in order to produce a depression which would cause an error of 1,000 with a substance of infinite molecular weight, 1,000 grams of the substance would have to contain a gram-molecule of the impurity. Such an error could be caused by 1.8 per cent of water, 4.6 per cent of alcohol, 7.4 per cent of ether, or an oxygen content of 1.6 per cent, of which more than 0.2 per cent is excluded by analysis.[245] Only hydrocarbons would then come into consideration as impurities—for example, 1.6 per cent methane, 6.8 per cent of isoprene, 13.6 per cent of limonene, 27.2 per cent of a diterpene, etc. Such amounts of volatile hydrocarbons as impurities are excluded by the constancy of weight in high vacuum at 40° to 50° C. Therefore, if criticism is to be directed against the cryoscopic method, whether because of the high colloidal state of rubber, gutta-percha, etc., or because of disagreement with the results of the osmotic pressure method, other points of attack, aside from the presence of impurities, must be sought.

One such point seems to be the lack of proof that the pure solvent crystallizes in these solutions or fusions and not perhaps solvates which behave abnormally and which make impossible the application of the laws of osmotic pressure.[246]

By Osmotic Rise Methods

K. H. Meyer and H. Mark,[247] as well as W. A. Caspari,[248] have studied solutions of rubber in benzene and in chlorobenzene according to the osmotic rise (capillary rise) method, using earthenware cells as membranes. With crepe rubber (nitrogen content 1.05 per cent) they found particles having

[243] *Z. angew. Chem.*, **42**, 79 (1929).
[244] *Ber.*, **61**, 1939 (1928).
[245] *Cf.* also Pummerer, Andriessen and Gündel, *Ber.*, **62**, 2635 (1929); *Rubber Chem. Tech.*, **3**, 487 (1930).
[246] *Cf.* Pummerer, *Kautschuk*, **5**, 129 (1929).
[247] *Ber.*, **61**, 1939 (1928).
[248] *J. Chem. Soc.*, **105**, 2139 (1914).

molecular weights of 346,000 to 378,000 in benzene and 186,000 to 264,000 in chlorobenzene. The values were somewhat smaller for alkali-purified crepe rubber (N content 0.54 per cent) namely 164,000 in chlorobenzene. Meyer and Mark consider these values as the micelle weights of the rubber in solution. H. Kroepelin and W. Brumshagen,[249] using collodion-coated Soxhlet thimbles as membranes, obtained values for the particle size of the same magnitude as the above, and arrived at the same conception of the particles as Meyer and Mark. The particles of sol-rubber obtained from acetone-extracted crepe were found to have molecular weights of 185,000 to 200,000 both at 11° C. and at 40° C.

The value of the molecular weight, M, was calculated for both temperatures from the formula

$$M = 22.41\ (1 + at) \cdot \frac{1}{(\frac{1}{c} - b)\ p}$$

Meyer and Mark calculated the constant, b, of the van der Waal equation as 0.03 to 0.04, explaining it as the actual volume (in 1 liter of solution) of one gram of the solvated osmotically active substance. Accordingly, one gram of rubber would combine with 20 to 40 grams of benzene in the solvate. Kroepelin and Brumshagen found 0.037 to 0.040 for b; but they point out the fact that b is not absolutely constant. The strong solvation which affects cryoscopic measurements must be regarded as decreasing the amount of available solvent, thereby causing too large depressions of the freezing points. For this reason, the values of 1,200 to 1,600 obtained in camphor by Pummerer are more nearly of the order of magnitude of the average value of 5,000 obtained by Meyer and Mark from x-ray results. Both of these values are uncertain. To decide these questions, it is necessary to examine the same solution by both the cryoscopic and osmotic pressure methods and thus to determine more exactly the sources of error in both methods.

According to Meyer and Mark, as well as Pummerer, rubber is an association colloid. The large particles having a molecular weight of 200,000 are regarded as micelles. In the transformation of rubber to hydrorubber, hydrocyclo-rubber, cyclo-rubber,[250] and rubber hydrochloride, the number of carbon atoms in the unit molecule remains essentially the same but the tendency for association no longer exists. For this reason, the hydrorubber solutions have a lower viscosity and can be filtered more easily.

A fundamentally different view is assumed by Staudinger. He thinks it possible that the rubber molecule itself possesses a molecular weight of the order of magnitude of 200.000. Hydrogenation and cyclization are, according to him, degradation reactions,[251] in which the molecular weight decreases to below 10.000. (*See* p. 228.) According to Staudinger[252] the "eucolloid" rubber gives rise to "hemicolloids." His conclusions are based upon extensive work with polyformaldehyde, polystyrene, and other large polymers. He regards the viscosity as a rather simple function of the molecular weight.

[249] *Ber.*, **61**, 2441 (1928).

[250] The products prepared with platinum and hydrogen below 100° C. are referred to here. The cyclization by heat is a more complicated process, which may involve simultaneous reactions of formation, decomposition, and rearrangement.

[251] According to Staudinger the addition of hydrogen chloride to rubber is accompanied by cleavage of the carbon chain (his assumption is based on the lowering of the viscosity as in the case of hydrogenation, which Pummerer attributes to the disappearance of the double bonds). The tendency towards cleavage is due to the ability of the rubber molecule to dissociate into radicals (*see* p. 188), according to Staudinger.

[252] In polyformaldehyde, Staudinger assumes that about 100 formaldehyde molecules are coupled through oxygen, corresponding to a mean molecular weight of about 4000.

From the relation between viscosity and molecular weight of the polystyrenes he draws analogous conclusions regarding the molecular weight of rubber and gutta-percha, for which he estimates values of about 100,000 and 50,000 respectively. The susceptibility of rubber solutions to heat (*see* p. 192) is also a property of the highly viscous polystyrene (which requires many years for its formation). Staudinger considers this property characteristic of the macromolecules. The fractionation of the polystyrenes yielded a series of polymers ranging from the lower, more soluble hemicolloids, the molecular weights (in the range of several thousand) of which could be determined in benzene, to the higher members, which were very viscous and had molecular weights too large to be determined.[253]

It seems very probable that in the same homologous series of polymers, the molecular weight can be roughly estimated from the viscosity only if pure hydrocarbons are concerned. Impurities containing oxygen or nitrogen have an overwhelming influence, however, even if they are present to the extent of only a few per cent (as in the case of raw rubber). Although it might seem desirable to draw conclusions regarding the rubber molecule from the work on polystyrene, or to deduce the size of the gutta-percha molecule from either that of rubber or polystyrene, such conclusions based on analogous experiments in different homologous series are nevertheless very unsafe.

In the case of rubber, association or aggregation plays, at most, a subordinate role according to Staudinger. However, the aging of rubber preparations, which is also manifested by an increase in the heat (negative) of swelling (*see* p. 478), is best explained as the result of aggregation or association.

The Chemical Constitution of the Rubber Molecule

The Ozone Reaction

As previously stated, the size of the rubber molecule has not been determined with certainty by physical methods. This is also true of the numerous chemical methods which have been tried, although a comprehensive knowledge of the structural principles of the rubber molecule has been developed.

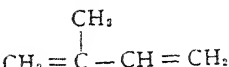
On p. 210, the important results of Harries' investigations on the ozone degradation of rubber were discussed. From these results it follows that the rubber molecule is principally built up by the addition of a number of penta-dienyl groups:

$$= \overset{\displaystyle CH_3}{\overset{|}{C}} - CH_2 - CH_2 - CH =$$

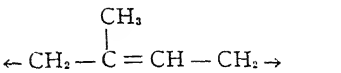
since only levulinic aldehyde and levulinic acid (formed by the oxidation of levulinic aldehyde) can be detected in the products resulting from the degradation with ozone. It also follows that the double bond which can be determined for each C_5H_8 group in rubber is attached to a methyl-substituted carbon atom. Therefore, as the above formula for the penta-dienyl unit shows, the rubber molecule is not formed from branched carbon chains. If the molecule is formed from isoprene units, it is probable that after polymerization the remaining double bond is situated between the two central carbon

[253] Staudinger states that hemicolloids of a molecular weight of 2000 to 10,000 never give highly viscous solutions. Concerning the polystyrenes, see *Ber.*, **62**, 241, 263, 442, 2909, 2912, 2921, 2933 (1929).

atoms, while the 1- and 4-carbon atoms serve as connecting links (Thiele's 1, 4 addition):



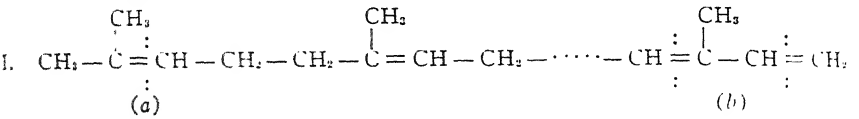
isoprene, independent molecule, before polymerization.



isopentene group, bivalent, dependent molecule, after polymerization.

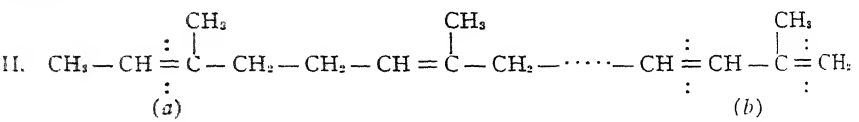
In the case of artificial rubber prepared from methylisoprene (2, 3-dimethylbutadiene), this displacement of the double bond during polymerization can be proved. Since only the ketone, acetonyl-acetone, is formed as a result of ozonolysis of this product, the double bond, after polymerization, must lie between the methyl-substituted carbon atoms.

These results of Harries on the degradation of rubber by ozone give no information about the molecular size of natural rubber or of artificial rubber, for it is not known how often the penta-dienyl group recurs in the molecule. Originally Harries assumed that two, later four, and finally six to eight isopentene groups existed in a large ring structure. An open-chain formula with a terminal isoprene group (*see also* p. 223):

I. 

in which the horizontal series of dots indicates an indeterminate number of isopentene groups, was early assumed by Weber and later adopted by Staudinger.[254] Harries rejected this formula because the terminal groups of such an open-chain molecule should yield acetone by cleavage at (a) and methylglyoxal by cleavage at (b) in the decomposition of its ozonide (at the points marked by vertical dots). These substances, which can be readily recognized, were never found among the decomposition products. It should be emphasized here that the highest yield of definite decomposition products obtained by Harries never exceeded 70 per cent of the theoretical quantity. This yield is too low to exclude arbitrarily the presence of any such terminal members.[255] The presence of acetone is easily determined both qualitatively and quantitatively,[256] but small quantities of methylglyoxal could more readily escape detection.

It is possible to formulate an open chain in which no acetone need be formed:

II. 

Acetaldehyde (or acetic acid) would be produced from the terminal group

[254] Staudinger and Fritschi, *Helv. Chim. Acta*, **5**, 785 (1922).

[255] His concluding experiment with 330 grams of raw rubber gave 53 grams of levulinic aldehyde and 248 grams of levulinic acid. "Unattacked" rubber to the extent of 30 grams remained from the ozonization, and 10.5 grams of resin resulted from the decomposition of the ozonide ("Untersuchungen ....," p. 116).

[256] Pummerer and Gerlach were able to detect traces of acetone (about 0.1%) in sol-rubber by the reaction with o-nitrobenzaldehyde (*Ber.* **64**, 817 (1931).

at (a) in this case, while methylglyoxal would be expected from the terminal group at (b), which is a differently oriented isoprene group. Harries usually performed the ozonization in ethyl acetate and therefore failed to observe the formation of acetic acid. By ozonization in chloroform and subsequent decomposition with water, appreciable amounts of this acid may be detected, according to Pummerer and K. Gerlach.[257] It is however questionable whether the acetic acid is not produced by a rearrangement (oxygen migration) of the rubber ozonide. Opposed to the second formula given for the open chain is the fact that open chain terpene-like products such as citral, phytol, and lycopin, usually have the following grouping at one end of the chain:

$$CH_3-\overset{CH_3}{\overset{|}{C}}<$$

Furthermore, the results of optical experiments do not indicate the presence of an isoprene system.

The Absorption Spectrum of Rubber in the Ultra-Violet Region

An important advance in the investigation of the rubber molecule was achieved in the systematic purification of rubber by means of alkali and by solvents, as carried out by Pummerer and his associates. The purification was carried to the point where the sample possessed optically constant absorption properties in the ultra-violet spectral region. The progress of the purification can be followed by the curves on p. 494. According to G. Scheibe and R. Pummerer,[258] the position and the intensity of the absorption are very similar to that of trimethylethylene (isopentene). Especially important is the fact that no evidence was obtained, according to optical measurements, for the presence of a conjugated system of carbon double bonds (isoprene groups) at the end of the chain. From the great accuracy of the method and the sharp decline of the curve for sol-rubber at $230m\mu$ ($\log K=0.7$), it may safely be concluded that no terminal isoprene group occurs in the molecule containing 500 double bonds (of the isopentene groups), and that probably no isoprene group is present for each 1,000 double bonds in the molecule of rubber. The extinction coefficient of isoprene at this wave-length ($\log K=4.2$) is 3,000 times as large as that of rubber.

The optical properties of rubber certainly verify the conclusion reached by Harries (on the basis of ozone degradation) that no open chain with a terminal isoprene group is present. For these reasons, and on the basis of the iodine number (see below), Pummerer[259] in 1927 expressed his opinion as follows: "Either a ring at the end of the chain has been formed, or the double bonds[260] of the terminal groups of several molecules have united, or else there was present originally a very large ring consisting of isoprene groups, according to the view of Harries. The existence of such rings composed of 32 carbon atoms (four eight-membered rings) can today be more readily accepted after the excellent work of Ruzicka."

Staudinger explains the failure to detect the end members by the assumption of an unusually long open chain consisting of about 1,000 isopentene groups, with a terminal isoprene group. Since the isoprene group makes up only 0.1 per cent of the total molecule, the products of the decomposition of

[257] *Ber.*, **64**, 809 (1931).
[258] *Ber.*, **60**, 2163 (1927).
[259] Lecture, Essen. *Kautschuk*, **3**, 233, 237 (1927).
[260] Or terminal isoprene groups.

this group on ozonolysis of the molecule could easily escape detection. Recently, Staudinger [261] is more inclined to accept a large ring formula upon the basis of analogous results on polystyrene. He supposes that the members of this formula are large rings composed of hundreds or even a thousand isopentene groups.

The Iodine Number of Rubber

Fisher and Gray [262] determined the iodine number of crude rubber by means of iodine chloride and found that the value for the unsaturation was 95 to 96 per cent of the theoretical value, which requires one double bond for each C_5H_8 group (theoretical iodine number = 373.4). From their work, as well as from the results of the action of ozone, of bromine, and of hydrogen chloride upon rubber, the isopentene group again appears as the "stoichiometrical equivalent" of rubber. These results, however, offer no information regarding the molecular size of rubber. It was therefore important to repeat the determinations of the iodine number with the purest rubber as well as with the individual fractions of pure rubber. Pummerer and Franz Josef Mann [263] determined the iodine numbers of total rubber and of sol-rubber and obtained values of about 101.3 per cent for the unsaturation of total rubber and 100.3 per cent for sol-rubber. The latter value indicates exactly one double bond for each C_5H_8 group. In the case of sol-rubber, prepared from crepe, the value is lower (97.6 per cent). If in this case the sol-rubber is a homogeneous substance having a monocyclic structure containing one double bond for each C_5H_8 group it would appear that partial cyclization of the molecule has also occurred.

Attention is called to the fact that a value of 100 per cent for the unsaturation of sol-rubber obtained by the "iodine number" method corresponds to a value of 94.6 per cent by the "oxygen number" method (reaction with perbenzoic acid, *see* p. 209).[264] From these values it is apparent that approximately 1 16 of the total number of double bonds do not react with perbenzoic acid. A corrected iodine number ("reduzierte Jodzahl") of about the same magnitude (93.6 per cent) results if from the original iodine number a correction is subtracted for the acid which is formed during titration (after addition of water). One mole of iodine is removed for each two moles of halogen acid. In the case of sol-rubber, water therefore removed about 1 16 of the total halogen which had reacted with the double bonds.[265]

Since it cannot be shown that sol-rubber consists of homogeneous molecules it is difficult to draw stoichiometrical conclusions from the above values. Again, since the reaction with perbenzoic acid is conducted at 0° C., it must be remembered that in some instances this reagent does not react with unsaturated compounds at 0° C. (Compare the behavior of limonene).[266] The remarkable agreement of the oxygen value with the "reduced" iodine number which was found with each of four sol- and gel-rubbers of different origins, can well have a constitutional basis.[267] In a uniform large ring system composed of isopentene groups, such a behavior is difficult to understand, but is more easily comprehended with a long chain such as II (p. 236), with terminal rings which resulted in some manner from the end isoprene groups.

[261] *Ann.*, **468,** 29 (1929).
[262] *Ind. Eng. Chem.*, **18,** 414 (1926).
[263] *Ber.*, **62,** 2636 (1929). See also p. 197.
[264] Pummerer and Franz Josef Mann, *Ber.*, **62,** 2636 (1929); Chem. Abstracts, **24,** 1103 (1930). See also p. 197.
[265] This suggests hydrolysis or cyclization. *Cf.* Staudinger, *Ann.*, **468,** 34 (1929).
[266] Concerning the iodine numbers and oxygen values of the carotinoids, see R. Pummerer, L. Rebmann, and W. Reindel, *Ber.*, **62,** 1411 (1929).
[267] In the case of carotin, the same agreement is also found, but it is not so distinct with guttapercha.

The oxygen number and the "reduced" iodine number of gel-rubber have values of 98.6 to 100 per cent and are higher than those for sol-rubber. The actual value for unsaturation, as determined by the iodine number, lies between 108 and 110 per cent. Since gel-rubber reacts differently toward iodine chloride than sol-rubber, the fractionation must have brought about some definite change. To explain the high iodine number, it could be assumed that for every ten isopentene groups there is present one additional double bond, such as would occur in a terminal isoprene group. The optical absorption, however, does not reveal a difference between sol- and gel-rubber great enough to indicate the presence of such an isoprene group. With sol-rubber, the dry solution after reaction with iodine chloride, contains no halogen acid. With gel-rubber, however, hydrogen chloride is present, which explains the high iodine value. If the halogen acid which is evolved when the reaction is performed in the absence of moisture, is due to substitution, then the value for the unsaturation of gel-rubber is reduced to between 98 and 99.6 per cent.[268]

The Structural Unit and the Parent Molecule of Rubber

It has been shown that most of the reactions of rubber indicate that the structural unit of the rubber molecule is the C_5H_8 group, which is able to add two univalent groups. The determination of this structural unit, adds nothing to our knowledge of the molecular weight, however. In order to determine the molecular weight, it would be necessary for the whole rubber molecule to react as one unit, as in the case of hemoglobin, in which only the one iron atom per molecule enters into reaction, or carotin, $C_{40}H_{56}$, which, despite its eleven double bonds, yields only the crystalline di-iodide, $C_{40}H_{56}I_2$, (prepared by Willstätter and Mieg) containing the smallest possible amount of iodine. The quantitative proof for the presence of one such terminal member or additional double bond for a definite number of isopentene groups would be of considerable importance; but this has not yet been accomplished.

Nitrosobenzene reacts in the ratio 1:1 with the C_5H_8 group of rubber. The molecular weight of the reaction product (*see* p. 204), which can be determined in nitrobenzene, indicates that union of eight isopentene groups with eight molecules of nitrosobenzene has occurred. Gutta-percha gives a similar analytically pure product which is composed of six isopentene groups and six nitrosobenzene molecules. The fact that a value twice the normal molecular weight of the nitrone of gutta-percha is obtained in benzene solutions in concentrations of 2 per cent and above, shows that the nitrone molecule is associated in this solvent. Therefore rubber and gutta-percha differ in other respects than the length of their carbon chains.[269] There must be present a sub-division or spatial period which is different in the two substances.

From results on the hot vulcanization of rubber a molecule of rubber composed of eight isopentene groups is indicated, according to Lindmayer.[270] There is a temporary pause in the absorption of sulfur after one atom of sulfur has been taken up by each unit of eight isopentene groups. From these experiments, a unit of eight isopentene groups can be considered as the parent molecule (that is, the simplest number of structural units which react as a unit molecule) of rubber. A maximum of four isopentene groups in rubber react with one tetranitromethane molecule. The same ratio allows

[268] Pummerer, *Kautschuk*, **5**, 130 (1929).

[269] *Cf.* Staudinger, *Ann.*, **468**, 30 (1929).

[270] *Kautschuk*, **5**, 35 (1929).

the reaction of two molecules of tetranitromethane with one unit of eight isopentene groups. By the hydrogenation of rubber, Pummerer and Koch have isolated a saturated hydrocarbon of some fifty carbon atoms (ten isopentene groups), but it was not certain whether decomposition of the hydrorubber had occurred. In general, the smallest parent molecule of rubber that can be discussed is, according to the above, the unit of eight isopentene groups. One usually finds higher values for the molecular weight of hydrorubber, hydrocyclo-rubber, and cyclorubber in camphor; namely, 1,000 to 2,000. On account of the possible sources of error in the cryoscopic method for the molecular weight determination (formation of solvates), K. H. Meyer and H. Mark consider it probable that these figures may be raised to about 5,000. Very high molecular weights of rubber and hydrorubber are rendered improbable by the solubility of these substances in ether, as well as by the low melting point of frozen and homogeneous crystallized rubber. The parent molecule of rubber is, according to our present idea, only a small fraction of the micelle, the presence of which can be established by osmotic rise measurements in benzene.

Synthesis and Artificial Rubber

Historical Development and General Discussion

Artificial Isoprene Rubber

The theoretical relationship between rubber and isoprene was apparent from the similar elementary composition of the two substances, as well as from the formation of isoprene by the distillation of rubber. Williams, the discoverer of isoprene, observed soon after its preparation (1860) that the oxygen of the air changed it in such a way as to increase its consistency.[271] Bouchardat, in 1879, undertook a more careful examination of the behavior of isoprene in air. He found that isoprene, upon standing, slowly changed to a rubber-like substance, and that the change, under certain definite conditions, took place more readily in the presence of hydrogen chloride gas. The data of Bouchardat, as well as those of Tilden, gave no definite experimental conditions by which it might have been possible for later workers actually to prepare artificial rubber. Tilden[272] himself says very pessimistically:

"The conversion of isoprene into rubber occurs, so far as observed, under two conditions: (1) when brought into contact with strong aqueous hydrochloric acid or moist hydrogen chloride gas, and (2) by spontaneous polymerization.

"In the former case, the amount of rubber produced is small, as it is only a by-product attending the formation of isoprene hydrochlorides, which are both liquid. In the latter case, the process occupies several years.

"Of course many attempts were made by me to hasten the process, but it was found that contact with any strong reagent, such as oil of vitriol, pentachloride of phosphorus, and others of milder character, led only to the production of a sticky 'colophene' similar to the substance which results from the polymerization of the terpenes, and after a course of experiments which were carried on for about two years, I was reluctantly obliged to abandon the subject."

[271] *Proc. Roy. Soc., (London)*, **10**, 516 (1860). [272] *India Rubber J.*, **36**, 322 (1908).

Later experiments with the use of hydrogen chloride never accomplished the desired result. The polymerization of isoprene in the cold was again investigated after the discovery that it could be polymerized with the aid of heat (*see* below). Harries later confirmed the fact that the beginning of the polymerization depends upon circumstances such as the presence of some oxygen as catalyst (*see* p. 258).

The action of light upon isoprene had previously been observed by Wallach in 1887. He found that isoprene was thus converted to a rubber-like mass.[273] In 1913, Harries prepared a white solid polymer by the action of ultra-violet light upon isoprene, but he obtained only a small quantity of a rubber-like product.

The chief uncertainty of the older data lies in the undefined expression "rubber-like properties." In the polymerization of unsaturated hydrocarbons by certain methods, products having properties which more or less resemble those of rubber are formed. Prior to Harries' work on the ozone degradation of rubber, these products could not be identified as artificial rubber, because of the lack of suitable methods. Harries first showed that the degradation of natural rubber by ozone proceeded in a fairly simple manner with the formation of considerable (about 60 per cent of the theoretical amount) levulinic aldehyde and levulinic acid. This represents a criterion which must be met by true [274] artificial isoprene rubber.

Ability to be vulcanized and elasticity of the vulcanizate are further requirements which must be satisfied, even though they do not definitely characterize the product. Moreover if the artificial product is to be termed rubber, its mechanical properties, especially after vulcanization, must conform to certain standards.

Finally, Harries considered the formation of rubber nitrosite C a specific reaction of rubber. He found in 1902 that isoprene, when heated to 300° C., yields not only dipentene and other hydrocarbons, but also thick, rubber-like syrups, which, in contrast to rubber distillate, give nitrosite C. The polymerization of myrcene (an open-chain terpene, $C_{10}H_{16}$, containing three double bonds) by heating for four hours at 300° C., produces a non-distillable polymyrcene and a dimyrcene which can be distilled *in vacuo*. Dimyrcene reacts with nitrous acid to form a nitrosite which cannot be distinguished from rubber nitrosite C, and which corresponds in composition and molecular weight to the formula $C_{20}H_{30}N_6O_{14}$. The polymyrcene nitrosite agrees with the formula $C_{40}H_{56}N_6O_{18}$ and is very similar to the dimyrcene nitrosite, although the polymyrcene, judging from the lower nitrogen content of its nitrosite, must be extensively cyclicized. The cyclization is easily explained today, by the high polymerization temperature employed. On the basis of these observations, Harries in 1902 inclined toward Weber's view that rubber is a long, open-chain polyterpene.

The fact cannot be ignored, however, that there is a great difference between dimyrcene and rubber, and that substances of the type of nitrosite C can be formed from higher open-chain terpenes other than rubber. It is, of course, very probable that the rubber molecule itself, in forming nitrosite C, has undergone degradation by nitrogen dioxide (analogous to the reaction with ozone), and that even dimyrcene nitrosite could finally be produced from rubber. At the present time, the formation of nitrosite C can still be regarded as desirable, but no longer sufficient, to identify a sample of artificial isoprene

[273] *Ann.*, **239**, 48 (1887).

[274] That is, possessing a constitution as closely related as possible to natural rubber, in order to deserve the name "synthetic rubber."

rubber. Although Harries, in 1902, had the express purpose of converting isoprene and myrcene into artificial rubber by polymerization with heat, he did not succeed in proving that he had accomplished his objective. Nevertheless, his polymerization experiments, which he never entirely abandoned, have given an important stimulus to the further study of the question.[275*]

Rubber chemistry was given the strongest impetus in 1904 by the work of Harries on the ozone reactions, which then occupied his time completely and diverted his attention from experiments on synthetic rubber. By means of his researches with ozone, the structure of the rubber hydrocarbon was in a general way cleared up, even if the finer details of the constitution were not solved at that time. The constant recurrence of the pentadiene group in rubber indicated the simple structural unit, isoprene, more categorically than did the decomposition by distillation.

These important degradation results, which made possible the actual characterization of a rubber substance, together with the rising price of rubber in 1909, greatly stimulated attempts to prepare artificial rubber. A far-reaching, even if not final, solution for this technical problem was accomplished in 1909 by Dr. Fritz Hofmann and his co-workers [276] in the Farbenfabriken vorm. Fr. Bayer and Co. He can therefore be called the actual discoverer of artificial rubber. The desired goal was reached by polymerization of isoprene with heat, both with and without dilution, under essentially milder conditions than those employed by Harries. In the first patents [277] (dated September, 1909, but of course made public much later) directions were given for heating isoprene for eight days at a temperature of 120° or 200° C. Later, (1910-1912) the duration of the reaction was increased and the temperature was lowered to less than 100° C. Numerous substances which acted as catalysts for the reaction were tested, and the greater part of them were protected by patent. In 1909, the Farbenfabriken sent a sample of artificial isoprene rubber to Harries, who, after investigating its behavior toward ozone, was able to pronounce the sample chemically similar to natural rubber. As accelerators for the polymerization, finished artificial rubber, natural rubber, and their oxidation products, play an important part.[278]

It was not long before Harries, in 1910, obtained artificial rubber by a modified process (longer heating of isoprene in acetic acid at 100° C. in a closed vessel) and issued the first publication on artificial rubber.[279]

The discovery that isoprene could be polymerized by means of metallic sodium to a substance similar to rubber (the so-called "sodium rubber") was also made in 1910, simultaneously and independently by Harries and by

(boiling point 63° to 63.5° 20 mm.) w polymerized to rubber by the action of metallic sodium and barium peroxide. *J. Russ. Phys. Chem. Soc.*, **47**, 1923, 1928, 1958 (1915).

* Translator's Note. G. S. Whitby and R. N. Crozier [*Can. J. Research*, **6**, 203 (1932)] have also investigated the polymerization of isoprene and 2,3-dimethylbutadiene by heat. They found no evidence of the formation from either diene of an open chain dimer, polymerizable to rubber, such as the "β-myrcene" of Ostromislensky. The above dienes yield oily, dimeric by-products in addition to rubber, and the proportion of oil to rubber increases with the temperature of polymerization. Isoprene yields more oily by-product than dimethylbutadiene. The degree of polymerization of the rubber obtained from the above dienes is applied.

[276] In this connection, see also page 268.

[277] German Pat., 250,690, Class 39-b-1 (September 12, 1909).

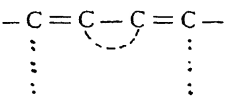
[278] See the patent literature. Also Lebedeff, *J. Russ. Phys. Chem. Soc.*, **45**, 1313, 1377 (1913), including a compilation of data concerning the speed of polymerization of various butadienes at 150° C.

[279] Lecture at Vienna, **1910.**

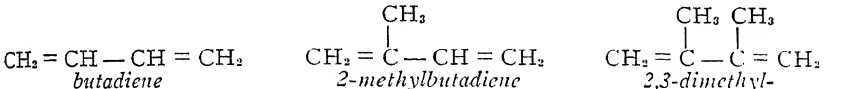
Matthews[280] and Strange in England. In contrast to the rubber produced by polymerization with heat and the rubber which was produced with the aid of heat and acetic acid, the sodium rubber behaved abnormally toward ozonization, since the ozonide on hydrolysis gave no levulinic aldehyde. A slight change in the process, namely, the polymerization by means of sodium in an atmosphere of carbon dioxide, was made by A. Holt[281] in 1914 in the laboratories of the Badische Anilin- und Sodafabrik.

This procedure yielded an artificial rubber which behaved normally upon degradation with ozone, although in contrast to isoprene rubber which was obtained by polymerization with heat, it was insoluble in the usual solvents.

The most important conclusions from the polymerization experiments with isoprene are here summarized in brief. The presence of conjugated double bonds (*see* page 223),



through which the mutual addition may proceed in various ways,[282] is essential for the polymerization of isoprene. The methyl group is not essential. Isoprene, butadiene, and dimethylbutadiene can form polymers.



butadiene — *2-methylbutadiene or isoprene* — *2,3-dimethylbutadiene*

Polymers can also be produced from 1-methylbutadiene or piperylene, $CH_3—CH=CH—CH=CH_2$, an isomer of isoprene. It is thus possible to produce polymers from the entire series of butadienes. These polymers may, because of one property or another, become commercially important. According to their properties, however, not all of these polymers, really deserve to be called artificial rubber. Some oily and pasty products are formed, the production of which must be avoided, if possible, in the preparation of artificial rubber.

Artificial isoprene rubber gives vulcanizates which are very elastic, but are only slightly resistant to tear. The best results were obtained by K. Gottlob by polymerization of isoprene in a water suspension of animal or vegetable proteins. The difficulty of obtaining the isoprene prevented this process from assuming commercial importance during the war.

Methyl Rubber

The methyl-homolog of isoprene, 2,3-dimethylbutadiene, was comparatively readily obtainable during the war. Therefore, when the scarcity of rubber in Germany became critical, a factory was built at Leverkusen for the manufacture of artificial methyl rubber; that is, rubber derived from di-

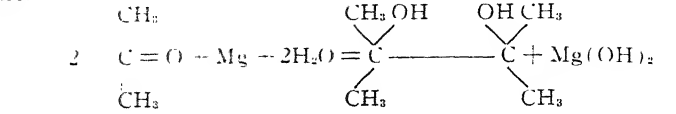
[280] See Harries: "Untersuchungen ..," p. 141, where Harries disputes the English and Russian claims of priority for the discovery of artificial rubber. In this connection, see also F. Hofmann: *Gummi-Zeitung*, **26**, 1794, (1912). It is common to all these claims that they were first brought forward after the preparation of artificial rubber by German chemists (part of them years later—Lecture by W. H. Perkin, Jr., 1912). There is no doubt that the artificial rubber which actually deserved the name and which was technically useful, was first produced in Germany. F. Hofmann and his co-workers have the priority over all their professional colleagues.

[281] *Chem.-Ztg.*, **38**, 188 (1914).

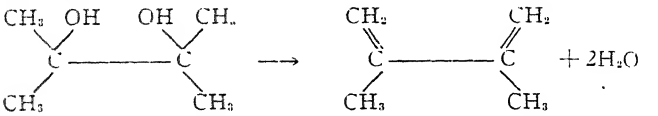
[282] For a discussion of the possible schemes of polymerization of isoprene, see G. S. Whitby, *Trans. Inst. Rubber Ind.*, **5**, 184 (1929).

methyl butadiene and containing for each C_5H_8 unit one more methyl group than in natural rubber.[283]

The starting material for the preparation of dimethylbutadiene is acetone, which is converted by means of magnesium or aluminum amalgam into pinacone.



This reaction is best carried out in an inert medium (benzene), and is followed by decomposition of the amalgam by means of water and dilute acid. Couturier,[284] in 1880, obtained dimethylbutadiene by heating pinacone with dilute sulfuric acid and removing two molecules of water, according to the following scheme:



Kondakoff devised a method starting with the corresponding dichloride of pinacone,[285] from which he eliminated two molecules of hydrogen chloride by means of alcoholic potash. Better technical methods of eliminating water were developed, such as heating with potassium bisulfate [286] or the catalytic removal of water by vacuum distillation over heated clay.[287]

Credit is due Kondakoff for important observations on the polymerization of dimethylbutadiene. He reported that in the action of alcoholic potash solution upon the hydrochloride of dimethylbutadiene at 150° C., a rubber-like, alcohol-soluble product was formed in addition to dimethylbutadiene. Since it was soluble in alcohol, it could not have been methyl rubber.

Another more important observation was made by Kondakoff who noticed that β-γ-dimethylbutadiene, when subjected to dispersed daylight in a closed vessel, gradually changed to a white, solid, polymerized mass, insoluble in the usual solvents.[288] According to the investigations of Harries,[289] this product is related to methyl rubber in some ways, but cannot be designated as methyl rubber. In contrast to a sample of methyl rubber prepared at 90° to 100° C. by Harries, the polymerized β-γ-dimethylbutadiene was converted into a tough, sticky mass upon short exposure to the air, giving a product which was easily soluble in the usual solvents and which was of no commercial value. Here lies the reason why Kondakoff's noteworthy observations remained temporarily without further effect upon the development of the chemistry of synthetic rubber.* Later work has frequently been connected with β-γ-dimethylbutadiene, which may be designated as the forerunner of artificial rubber. In Leverkusen, conditions were found under which this substance

[283] Butadiene rubber, prepared from sodium according to the method of Matthews and Strange, had gained the most attention in England, in 1910. Small amounts of this rubber were prepared there, in 1914, on an experimental scale. The butadiene was obtained from *n*-butanol by way of butene (*see* p. 250).

[284] *Bull. soc. chim.*, (3) **33**, 454 (1880); *Ann. Chim.*, (6) **26**, 485 (1892).

[285] *J. prakt. Chem.*, (2) **62**, 169 (1900).

[286] Procedure used commercially by the Farbenfabriken vorm. Friedrich Bayer & Co.

[287] German Pat., 235,311, Class 12o, 19 (1910); 256,717, Class 12o, 19 (1912).

[288] *J. prakt. Chem.*, (2) **62**, 166 (1900); (2) **64**, 109 (1901). German Pat., 248,399, Class 39b.

[289] "Untersuchungen ..." p. 137.

* Translator's Note. Kondakoff's disagreement with these statements is expressed in an article entitled "The History of Rubber" *Rev. gén. caoutchouc*, **7**, No. 65, p. 6 (1930).

could be converted into a plastic, rubber-like mass,[290] by heating at 80° to 100° C.[291]

Commercial methyl rubber was prepared during the war by the Farbenfabriken vorm. Friedrich Bayer & Co. by means of two fundamentally different methods, which produced two distinct final products: methyl rubber H, used especially for hard rubber goods, and methyl rubber W, for soft rubber goods.[292] (*See also* p. 17 ff.)

Methyl rubber H was produced by placing dimethylbutadiene in thin-walled metal vessels in such a way that an air space remained above the liquid. The drums were stored at approximately 30° C. for six to ten weeks, during which time the container became filled with the polymer, which was formed as a white, solid mass having the appearance of cauliflower, and having a crystalline appearance. After the disappearance of the liquid by polymerization, the drums were cut open, and the mass, having little of the appearance of rubber, was converted to rubber sheets by prolonged milling, with or without the addition of softeners and preserving agents. The polymerization could be controlled more easily by the addition of catalysts, such as some of the final product.

For the production of methyl rubber W, dimethylbutadiene was placed in double-walled pressure vessels, and large charges were heated for three to six months at about 70° C. The vessel then contained a slightly yellow, transparent, rather tough, rubber-like mass, which had to be cut from the containers in thin layers by special rotating knives. This product was then placed upon the mixing mill as described above. Methyl rubber W was used especially for the preparation of soft rubber goods, either alone or mixed with a portion of natural rubber or methyl rubber H.

The monthly production of artificial rubber in the later years of the war is given by Gottlob [293] as 150 tons, and the total production of artificial rubber during the war as 2,350 tons.

The sensitivity of both unvulcanized methyl rubbers toward oxygen is much greater than that of natural rubber. This difference is intensified by the action of light. The methyl rubbers were therefore colored with suitable dyes in order to absorb the damaging light rays in the outer layers. This procedure also increased the stability of the rubbers toward air. Other preserving materials were also used. By the addition of aromatic bases and other softeners to the rubber compounds, the elasticity of the vulcanizates was increased at the expense of the resistance to tear.

Methyl rubber W was at best not a very desirable substitute for soft rubber goods, and would in normal times disappear from the market. On the other hand, methyl rubber H, when worked up into hard rubber goods, showed exceptional insulating and dielectric properties, which even surpassed those of the usual hard rubber. At a price which compared favorably with that for hard rubber, it would be competitive for this purpose. However, the method employed during the war for the preparation of methyl rubber from

[290] See also Lecture by F. Hofmann: "Der synthetische Kautschuk vom technischen Standpunkt," given May 30, 1912 in Freiburg. *Z. angew. Chem.*, **25**, 1462 (1912).

[291] German Pat., 254,668, Class 39b, 1 (March 15, 1912). The irregular behavior of Kondakoff's substance toward ozone was not altered to correspond with methyl rubber by this further treatment, according to Harries, "Untersuchungen ...," page 200.

[292] See also K. Gottlob, "Acht Jahre Arbeit am künstlichen Kautschuk, der Methylkautschuk im Kriege." *Gummi-Ztg.*, **33**, 508, 534, 551, 576, 599 (1919) and Gottlob, "Technologie der Kautschukwaren," p. 211 to 214, 2nd ed. Verlag Vieweg u. Sohn, Braunschweig, **1925**, or the English translation, Gottlob, "Technology of Rubber" translated by J. L. Rosenbaum, McLaren & Sons, Ltd., London, **1927**.

[293] Gottlob, "Technologie der Kautschukwaren" p. 214, Vieweg u. Sohn, Braunschweig, **1925**.

acetone is out of the question today because of the current low prices of rubber, which can be further lowered by the plantations.

G. S. Whitby* and M. Katz [*Can. J. Research*, **6**, 398 (1932)] compared the properties of methyl rubber with those of natural rubber. "Samples of synthetic rubber prepared by the polymerization of 2,3-dimethylbutadiene at room temperature and at 45° C. respectively were subjected to vulcanization tests in comparison with natural rubber. In an accelerated gum stock containing 3% sulphur the cold polymer gave at best vulcanized products less than one-third as strong and only about one-third as extensible as natural rubber: the heat polymer gave products as extensible but only one-tenth as strong as natural rubber. The incorporation of carbon black greatly increased the strength of the synthetic rubbers, rendering both about half as strong as natural rubber in a similar stock. The vulcanized synthetic rubbers were less "snappy" than natural rubber at room temperature. Increase of temperature improved their speed of retraction, but seriously reduced their breaking strength. Products from the cold polymer showed a greatly increased stiffness and strength at 5° C. as compared with room temperature, and at about 1° C. were non-retractible. In general the synthetic rubbers were much more sensitive than natural rubber to change of temperature. A 50:50 mixture of the heat and cold polymers was also subjected to tests."

The Present Status of the Artificial Rubber Question†

The researches on the preparation of artificial rubber which are being conducted at the present time are justified for several reasons.

1. Methyl rubber H demonstrated that natural rubber can be surpassed in certain properties by the artificial product. The possibilities in this respect are far from being exhausted. It was emphasized on page 243 that the entire series of butadienes is capable of polymerization. The reaction can proceed in various ways with each individual hydrocarbon, and the final product can be influenced by the addition of various substances, such as nitrogenous compounds. It is therefore reasonable to expect the formation of a large number of artificial products, which could be used as artificial rubber for special purposes, or might be used for other purposes.

The final goal—the practical preparation of natural rubber itself by synthetic means—will not be attainable, or may only result accidentally, as long as the constitution of rubber has not been absolutely determined. The synthetic rubbers thus far prepared are artificial products with properties only more or less similar to those of rubber. Tremendous progress has been made since the war, however, in improving the properties of the artificial product so that it nearly resembles rubber, but much more development is possible. The variation of catalysts and of the conditions of polymerization are the most promising lines of work. In this connection, it should be stated that it has been possible recently to polymerize ethylene and its homologs in a very simple manner, to give substances of high molecular weight having the properties of lubricating oils.[294] For this purpose, boron trifluoride was used as a catalyst. The polymerization of vinyl bromide to form rubber-like substances was investigated by Ostromislensky[295] some years ago. His polymer, cauprene bromide, was a white, amorphous substance which, according to Harries, corresponded very well with the empirical formula, $C_8H_{12}Br_4$, but was distinctly different from the tetrabromide of butadiene rubber, and therefore undoubtedly belongs to another series of compounds. By reduction

* Translator's Note.

† Translator's Note. Two excellent reviews on synthetic rubber have recently appeared. See F. Jacobs, *Rev. gén. caoutchouc*, **9**, No. 81, 19; **9**, No. 82, 3; **9**, No. 83, 9 (1932); also G. S. Whitby and M. Katz, *Ind. Eng. Chem.*, **25**, 1204, 1338 (1933).

[294] M. Otto, *Z. angew. Chem.*, **40**, 700 (1927).

For the sake of completeness, it should be mentioned here that certain other hydrocarbons, such as cyclopentadiene, styrene, and indene can be polymerized to give synthetic products which have certain uses.

[295] *Chem. Zentr.*, **83**, (I), 1980, 1982 (1912); *J. Russ. Phys. Chem. Soc.*, **44**, 204, 240 (1911).

(debromination) of cauprene bromide, Ostromislensky obtained a practically halogen-free hydrocarbon of high molecular weight.

2. The strongest stimulus for the resumption of the synthesis of rubber was the anticipated reduction in price of the starting material, butadiene. There is no reason, therefore, at the present time for discussing in detail the numerous syntheses of butadiene and the methylbutadienes, which have been so carefully developed by the methods of organic chemistry. Harries [296] has given an excellent survey of these processes, and in the "Special Part" to follow, they will be briefly enumerated, with literature references (*see* p. 249).

One commercially important synthesis depends upon the production of isoprene from the pentane fraction of petroleum, through a series of reactions discovered by A. Holt in the Badische Anilin- und Sodafabrik.[297] The progress made in cracking processes has made the benzine hydrocarbons and the pentanes more readily obtainable. It should also be possible to effect catalytic refinements and thus lower the cost of Holt's process.

Aside from the production of butadiene from the pentane fraction of petroleum, there is the further commercial possibility of producing butadiene or its homologs directly by hydrogenation of carbon or carbon monoxide. It should at least be possible by the latter method to prepare fractions which can be easily converted to members of the butadiene series. There exist the further possibilities of preparing butadiene by the dehydrogenation of butane, or from aldol which is prepared synthetically from acetaldehyde. In view of the foregoing statements, it is easier to conceive of an improved artificial rubber being competitive with natural rubber. It will be some time before the synthetic product can be produced at a price lower than that of present natural rubber, which is estimated at 60 to 80 pfennig per kilogram. Synthetic rubber of especially high-grade properties could conceivably command a higher price than natural rubber, in which case the best would still be the most economical. It must be remembered, however, that constant progress has also been made in the cultivation of high grade *Hevea* strains and in the improvement of the quality of the natural product by better methods of preparation. Progress has also been made in the use of guayule in rubber mixes. Whatever the outcome of the contest between the product of the plantation and that of the chemist engaged in synthesis, organic chemical technology has scored a lasting triumph in making more accessible the members of the butadiene series. The availability of butadiene and its homologs has led to promising experiments for the purpose of preparing other synthetic products from butadiene. In this connection, attention is called to the work of Diels,[298] who studied the addition of butadiene to a wide variety of unsaturated cyclic hydrocarbons.

A new synthetic rubber* has recently been developed by Carothers, Williams, Collins, and Kirby,[299] in the laboratories of E. I. du Pont de Nemours & Co., Inc. The new product has been given the name "Duprene." The synthesis of this artificial rubber proceeds from acetylene, which is polymerized to monovinylacetylene, $CH{\equiv}C{-}CH{=}CH_2$. The monovinylacetylene is then treated with hydrochloric acid in the presence of cuprous chloride as a catalyst. The mechanism of the addition of HCl to vinylacetylene[299a] consists, first, in the addition of hydrogen chloride in the 1,4-position with the formation of

[296] "Untersuchungen ...," p. 142 ff.

[297] *Chem.-Ztg.*, **38**, 188 (1914); See also German Pat., 264,008, Class 120, granted to the Badische Anilin- und Sodafabrik.

[298] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

* Translator's Note.

[299] *J. Am. Chem. Soc.*, **53**, 4203 (1931); see also, J. A. Nieuwland, W. S. Calcott, F. B. Downing and (1931).

[299a] W. H. Carothers, G. J. Berchet and A. M. Collins, *J. Am. Chem. Soc.*, **54**, 4066 (1932); *Rubber Chem. Tech.*, **6**, 121 (1933).

chloro-4-butadiene-1,2. This readily undergoes isomerization to chloro-2-butadiene-1,3. Cuprous chloride facilitates the isomerization and no chloro-4-butadiene-1,2 is found in the reaction product when the above copper salt is used as catalyst. The reaction proceeds according to the following equation:

$$CH \equiv C- \quad :=CH_2- \quad {}_2=C=CH-CH_2Cl \xrightarrow{HCl} {}_2=\underset{\displaystyle Cl}{\overset{|}{C}}-CH=CH_2$$

The chlorobutadiene is known as "chloroprene," and is a colorless liquid with characteristic ethereal odor somewhat resembling ethyl bromide. It has a boiling point of 59.4° C. at 760 mm. pressure, a density, d_{20}^{20}, 0.9583, and refractive index n_D^{20}, 1.4583. The structure of chloroprene was established through its analytical composition, and by conversion into butane-α, β, γ, δ, tetracarboxylic acid and into β-chloroanthraquinone.

Chloroprene readily undergoes polymerization. Thus, if the chloroprene is allowed to stand in a closed container it polymerizes spontaneously and after 10 days has changed into a transparent, resilient, non-plastic, elastic mass resembling vulcanized soft rubber. This product is called μ-polychloroprene. It has a density at 20° C. of about 1.23, and a refractive index of about 1.5512 (n_D^{20}). The new product is not plastic and does not sheet out smoothly on the mill. Furthermore, it is not thermoplastic, and does not dissolve in carbon tetrachloride, carbon disulfide, benzene, nitrobenzene, pyridine, aniline, ethyl acetate, and ether, although these solvents do swell the product. It has a tensile strength of about 140 kg./sq. cm. and an elongation at break of about 800 per cent. The X-ray diffraction pattern of unstretched samples of polychloroprene shows an amorphous ring, but the stretched polymer exhibits a fiber diagram. In this latter respect, the μ-polychloroprene differs from previously described synthetic rubbers.

Analysis of the μ-polychloroprene indicates the composition (C_4H_5Cl) but molecular weight determinations are not possible, since the polymer is insoluble in the usual organic solvents. Towards bromine, the polymer behaves as an unsaturated compound. Nitric acid oxidizes it to succinic acid. The degradation with ozone has not been carried out. In this connection it should be noted that polychloroprene resembles vulcanized rather than unvulcanized rubber.

By interrupting the polymerization before completion, an α-polymer of chloroprene can be obtained. This product differs from the μ-product and is soft, plastic and soluble in benzene. The *alpha* product resembles unvulcanized rubber in its physical properties and mechanical behavior. It swells in benzene to give highly viscous solutions. At 30° C., the plastic α-polymer gradually changes into the elastic μ-polymer, and at 130° C. the change is complete in 5 minutes. Sulfur is not necessary to bring about the change from the α- to the μ-polymer. The change from the lower to the higher polymer corresponds to the vulcanization of natural rubber. Many catalysts, such as zinc oxide, zinc chloride, ferric chloride, and primary aromatic amines (aniline, benzidine, etc.) accelerate the vulcanization of the α-polymer, while secondary amines, which are among the best anti-oxidants for natural rubber, function as inhibitors of vulcanization.

It is interesting to note that chloroprene can be readily emsulsified in water with the aid of an emulsifying agent such as sodium oleate. The emulsified chloroprene polymerizes very rapidly and completely, but the resulting polymer remains suspended and constitutes an artificial latex resembling the latex of natural rubber. The artificial latex can be stabilized with ammonia, which prevents coagulation due to the acid formed during polymerization. I. Williams and H. W. Walker [*Ind. Eng. Chem.*, **25**, 199 (1933)] have shown that the polymerization in emulsions of the chloroprene-in-water or water-in-chloroprene type with oriented polar dispersing agents, such as sodium oleate, proceeds rapidly to μ-polymer. The nature of the polar interfaces and their distance apart appears to be the prime factor in causing the rapid polymerization of these emulsions and not to the increased surface of accelerating action of the dispersing agent.

A granular polymer (ω-polymer) has also been obtained from chloroprene. The formation of this polymer is initiated by light of 3130 Å. wave length. The ω-polymer is formed as a white, coherent mass of hard granules. It is non-plastic and shows no tendency to imbibe solvents.

Bromoprene has also been polymerized [W. H. Carothers, J. E. Kirby and A. M. Collins, *J. Am. Chem. Soc.*, **55**, 786, 789 (1933); *Rubber Chem. Tech.*, **6**, 323 (1933)] and behaves similarly to chloroprene. Four distinct polymers of bromoprene have been obtained, namely, the plastic α-polymer, the volatile liquid β-polymer, the granular ω-polymer, and the final product μ-polybromoprene. These polymers are analogous to the corresponding chloroprene polymers.

Carothers and Coffman[300] have extended the investigation on the polymerization of chloroprene to homologs of chloroprene. The rate of polymerization of chloroprene was found to be only slightly affected by the introduction of a methyl group at the 3-position (Chloro-2-methyl-3-butadiene-1,3). The dimethylchloroprene, chloro-2-dimethyl-3,4-butadiene-1,3, polymerizes very much more slowly than chloroprene and not much faster than isoprene. Chloro-2-tetramethylene-3,4-butadiene-1,3 also polymerizes very slowly. The authors reach the conclusion, that the methyl group is not an activating group, since butadiene, isoprene and β, γ-dimethylbutadiene polymerize spontaneously at about the same rate. Since chloroprene, however, polymerizes about 700 times as fast as isoprene, the chlorine atom has a powerful activating effect. From the respective rates of polymerization of 3-methylchloroprene and 3,4-dimethylchloroprene the retarding effect of a methyl group in the 4-position is shown.

The rate of vulcanization of chloroprene plastic polymer, and the state of vulcanization and physical properties of the vulcanizates are affected by metallic oxides, such as zinc oxide and magnesia, by small amounts of sulfur and by certain acid softeners such as rosin. The best results are obtained when the above materials are used in specific combinations with one another. [E. R. Bridgwater and E. H. Krismann, *Ind. Eng. Chem.*, **25**, 280 (1933)].

The resistance of Duprene to oils, acids, alkalies and other chemicals has also been studied [O. M. Hayden and E. H. Krismann, *Ind. Eng. Chem.*, **25**, 1219 (1933); see also E. R. Bridgwater, *Ind. Eng. Chem.*, **26**, 33 (1934)].

Considerable work on synthetic rubber has been done in Russia. It has been reported that four factories for the manufacture of synthetic rubber are now in operation in Russia and that two other plants are under construction. The basic raw material which is being used for the manufacture of the synthetic rubber is alcohol derived from potatoes. Recently it was announced that a new process had been worked out for obtaining alcohol from peat. A method for making synthetic rubber from acetylene has also been announced. The latter synthetic rubber is reported to excel synthetic rubber obtained by other methods. Extensive details of the method used in preparing synthetic rubber in Russia have not been published. The following is quoted from *Rubber Age (N. Y.)*, **34**, 171 (1934):

"Definite progress in the production of synthetic rubber in Russia was made during 1933, according to authoritative reports from Moscow. Attention has been devoted chiefly to butadiene rubber, of which hundreds of tons have been made. Tires from such rubber are said to have given mileages up to 27,000 kilometres on Russian roads, and a large new factory for the production of the rubber is being built at Yaroslav.

"The butadiene is made by a method developed by Lebedeff, which consists in passing ethyl alcohol under a slightly reduced pressure over a mixed dehydration-dehydrogenation catalyst, such as a mixture of alumina and zinc oxide. The yield is stated to be 20 per cent (34 per cent of the theoretical). Butadiene is isolated from the reaction products by absorption in kerosene or turpentine, after first cooling to — 5° C. in order to remove higher boiling material.

"Semi-large scale work is in progress on the recovery of butadiene from gas, obtained by the pyrolysis of oil, which is supplied to Leningrad and Moscow. Polymerization of butadiene in 70 per cent concentration is effected by means of metallic sodium. It is stated that the synthetic rubber has a wider temperature interval of elasticity than natural rubber; it will suffer lower temperatures without hardening, and at temperatures up to 80° to 100° C. it does not soften, but rather becomes somewhat harder. It can be reclaimed like natural rubber."

Special Part

Methods for the Preparation of Butadienes

A description of the methods for the laboratory and commercial preparation of the butadienes is beyond the scope of this book. The most important methods of formation, methods of preparation, and literature references, will, however, be outlined briefly.[301]

Butadiene, $CH_2=CH-CH=CH_2$

[300] *J. Am. Chem. Soc.*, **54**, 4071 (1932).

[301] Details of the preparation of the butadienes and their polymerization products are given in S. P. Schotz, "Synthetic Rubber," Ernest Benn, Ltd., London, **1926**, where numerous illustrations of the apparatus used are also given.

1. Erythrite is heated with formic acid (butadiene is therefore called erythrene).[302]

2. N-methylpyrrolidine[303] or aminocyclobutane[304] is exhaustively methylated to produce very pure products.

3. Mixtures of acetylene and ethylene are passed through heated tubes, giving butadiene, according to Berthelot.[305]

4. In the Elberfelder process (method of preparation),[306] phenol is hydrogenated to hexahydrophenol and oxidized to adipic acid with opening of the ring. The diamide of adipic acid, when subjected to the Hofmann reaction, gives 1,4-butylenediamine. Exhaustive methylation and distillation of the di-quaternary ammonium base gives butadiene.

5. According to Harries,[307] secondary butyl alcohol is converted to butene, then to butene dibromide, which is decomposed with heated soda-lime into butadiene and two mols of hydrogen bromide (method of preparation). Matthews and Strange proceed from primary butyl alcohol which is obtained by fermentation. Elimination of water gives 1,2-butene, the catalytic rearrangement of which gives 2,3-butene, etc.[308]

6. Acetaldehyde is converted to aldol, which is then hydrogenated with the splitting off of water.

7. By the hydrogenation of coal and carbon monoxide under certain conditions, the lower members of the saturated and unsaturated hydrocarbon series are produced in large quantities. This process offers a cheaper method for obtaining butadiene and isoprene.

Isoprene (2-methylbutadiene)

1. Tilden[309] discovered that isoprene could be formed by the distillation of rubber or by passing turpentine vapors through red hot tubes (method of formation).

2. Turpentine oil or limonene is decomposed in the vapor phase in contact with a heated platinum gauze (isoprene lamp), according to Harries,[310] or in vacuum, according to Staudinger and Klever.[311] By the latter modification, the yield is raised from 40 per cent to 60 per cent. Commercially, this method is too expensive. It is a convenient laboratory process, but does not yield a completely pure product.

3. A laboratory method for the preparation of the purest isoprene involves the conversion of 2-methyltetramethylene-1,4-glycol[312] to the corresponding dibromide, followed by treatment with tertiary bases.

4. The Elberfelder process of F. Hofmann and K. Coutelle starts with para-cresol, which is hydrogenated to methylcyclohexanol, from which methyl adipic acid is obtained by oxidation. The diamide of this acid is converted to the diamine, which is exhaustively methylated as in the preparation of butadiene. Distillation of the di-quaternary base gives very pure isoprene.[313]

5. By the process of Merling, acetylene is condensed with sodium acetone and the resulting methyl butinol is hydrogenated to methyl butenol, from

[302] Henninger, *Ann. chim.*, (6), **7**, 216 (1886); Charon, *Ann. chim.*, (7), **17**, 234 (1899).
[303] G. Ciamician and P. Magnaghi, *Gazz. chim. ital.*, **15**, 485 (1885); *Ber.*, **18**, 2080 (1885).
[304] *Ber.*, **38**, 1992 (1905).
[305] *Ann. chim.*, (4), **9**, 466 (1867).
[306] Ger. Pat., 231,806, Class 12-o (1909); *Friedländer*, "Fortschritte . . . .," **10**, 1014.
[307] Harries, "Untersuchungen . . . .," p. 164, 165.
[308] Schotz, *loc. cit.*, p. 124.
[309] *Chem. News*, **46**, 120 (1882); *J. Chem. Soc.*, **45**, 410 (1884).
[310] Harries and Gottlob, *Ann.*, **383**, 228 (1911) and Harries, "Untersuchungen . . . .," p. 142.
[311] *Ber.*, **44**, 2212 (1911).
[312] C. Harries and K. Neresheimer, *Ann.*, **383**, 167 (1911).
[313] Ger. Pat., 231,806, Class 12-o (April 9, 1909).

which isoprene is formed by the elimination of water.[314] This is an excellent complete synthesis.

6. The conversion of isopentene dihalides into isoprene was studied by Ipatiew[315] and Harries,[316] and extended to the entire pentane fraction of petroleum by A. Holt, in the laboratory of Badische Anilin-und Sodafabrik.[317] The latter commercial process is especially noteworthy today because of improved cracking processes, and also because it shows the relation between normal pentane and isoprene.

Isoprene prepared by the various methods shows very different degrees of purity.[318]

The purest isoprene* prepared by Harries and Neresheimer, according to the above method 3, by means of trimethylamine, has a boiling point of 33.5° to 34° C., specific gravity (21°) = 0.6804; refractive index ($D/21°$) = 1.42267. The Elberfelder isoprene obtained according to method 4 is just as pure.

Piperylene (1-methylbutadiene)

Up to the present time, this compound has received less attention than any enumerated in this section.

1. A. W. v. Hofmann[319] showed that piperylene is obtained by the exhaustive methylation of piperidine.

2. Ethylmagnesium bromide is added to acrolein, and water is eliminated from the resulting pentenol by means of phthalic anhydride, according to Harries and Schönberg.[320]

3. Two mols of ethylmagnesium bromide are added to ethyl formate, and water is eliminated from the resulting diethylcarbinol to produce pentene. Pentene dibromide is then formed, and 2 mols of hydrogen bromide are removed to obtain piperylene.[321]

2,3-Dimethylbutadiene

The starting material is pinacone, which is readily obtained by the reduction of acetone with magnesium amalgam or aluminum amalgam.[322] The removal of two mols of water (see p. 244) takes place in one step, according to F. Hofmann, Meisenburg, and Delbrück, when pinacone vapors are passed over heated potassium bisulfate; or when the vapors are passed over heated clay in a vacuum, according to a patent of the Badische Anilin -und Sodafabrik.[323] The earlier methods of Couturier (heating with dilute sulfuric acid) as well as those of Kondakoff and of Harries, which utilized the dichloride of pinacone, can today be considered commercially obsolete.

[314] Ger. Pat., 246,241, Class 12-o (1910); *Friedländer*, "Fortschritte . . . . ," **10**, 1013.
[315] *J. prakt. Chem.*, (2), **55**, 4 (1897).
[316] Ger. Pat., 243,075 and 243,076 (1910).
[317] Ger. Pat., 275,199; *Friedländer*, **11**, 808 and Ger. Pat., 263,017; *Friedländer*, **11**, 810 (1912); Ger. Pat., 264,008 (1911); *Friedländer*, **11**, 807; *cf.* also, Holt, *Chem.-Ztg.*, **38**, 188 (1914).
[318] *cf.* Harries, "Untersuchungen . . . .," Table on p. 161.
* Translator's Note. H. J. Waterman and H. A. Van Westen [*Rec. trav. chim.*, **48**, 1084 (1929); *Chem. Abstracts*, **24**, 824 (1930)] have determined the properties of pure isoprene. The following constants are given: b.p.$_{762}$ 34.5°-35.0° C.; d^{20}, 0.6806; N_D^{20}, 1.4194, mol. refraction, 25.29.
[319] *Ber.*, **14**, 665 (1881).
[320] *Ann.*, **395**, 243 (1913).
[321] *Rec. trav. chim.*, **25**, 206 (1906); *Chem. Zentr.*, **77**, II, 748 (1906).
[322] *Rec. trav. chim.*, **25**, 206 (1906); *Chem. Zentr.*, **77**, II, 748 (1906).
[323] Ger. Pat., 235,311, Class, 12-o, 19 (1910); Ger. Pat., 256,717, Class, 12-o, 19 (1912).

Polymerization of the Butadienes and the Ozone Degradation of Artificial Rubber

Introduction

Harries has made a contribution of considerable scientific and technical importance in classifying the artificial rubbers. Such a classification is difficult because reactions of fundamentally different types are involved in the formation of artificial rubber. For example, polymerization by one method leads to the formation of carbon linkages with the double bonds in the 1,4-position (normal rubber), while polymerization according to another method (sodium process) produces polymers with a different orientation of double bonds, accompanied perhaps by partial cyclization of the molecule. The problem is further complicated by the fact that artificial rubbers, polymerized by the same method, may differ in the degree of polymerization and therefore in the size of the unit molecules. This phase of the problem is not well understood. Again, synthetic products which in their chemical nature are of the same polymeric type, may differ in their colloidal nature and degree of association. Another factor greatly influencing the properties of the reaction product is the particular butadiene (methylbutadiene, etc.) chosen for polymerization. Finally, polymerization proceeds to varying extents, so that in any one product we are dealing with a mixture of polymers differing in degree only, as in the case of natural rubber. Under certain conditions, the products may have their properties so changed by traces of admixed oxidation products that they are no longer recognizable as synthetic rubber.[324] For this reason, only analytically pure synthetic rubber samples can serve for the degradation and for the determination of the fundamental properties of a certain class.

Staudinger[325] established the interesting fact that dust-free, polymerized isoprene rubber, prepared with extreme care, is optically void (Tyndall phenomenon) under the ultra-microscope. In all probability, the luminosity observed with natural rubber is due to contamination with foreign substances.

According to Harries, the term "normal" synthetic rubber is applied to those substances which have the same structural plan as natural rubber. They therefore contain one double bond for each butadiene or methylated butadiene, and are degraded by ozone in such a way that 1,4-dicarbonyl compounds are formed (in the case of isoprene rubber, levulinic aldehyde or its oxidation product, levulinic acid $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$ (*see* p. 212).

After the decomposition of the ozonide, these 1,4-dicarbonyl compounds, such as levulinic aldehyde, succinic dialdehyde, and acetonylacetone, are easily recognized by means of the pyrrole reaction, which produces a red color on a pine splint introduced into the vapors obtained by heating the solution containing the decomposition products with ammonium acetate.[326] The prerequisite for the formation of 1,4-dicarbonyl compounds is the recurrence of a double bond after each fourth carbon atom in a carbon chain.

[324] Compare Harries, "Untersuchungen ....," p. 173.

[325] Address, Düsseldorf. *Ber.*, **59**, 3019 (1926).

[326] Methylpyrrole is also formed from levulinic aldehyde and ammonia with the loss of two molecules of water.

If the double bonds are otherwise situated, or are removed by ring closure (cyclization), an abnormal rubber results. These changes are recognized by a decrease in the number, or by the total absence, of 1,4-dicarbonyl compounds. In this case the pyrrole test is faint or negative. Other decomposition products are then formed instead of 1,4-dicarbonyl compounds and these have not been identified, for the most part, and are largely included under the term "resin," although some of the products may actually be formed as resins.

The expression "normal," when applied to artificial rubber, therefore implies that its structure, in general, is analogous to that of natural rubber. Since we learn nothing regarding the size of the rubber molecule from the ozone degradation, differences in molecular size may also exist even between various normal polymers of the same butadiene (*see* polymerization by heat, and by sodium and carbon dioxide).

Harries employed the reaction with bromine (the so-called tetrabromide method), and the formation of nitrosite C, for the characterization of artificial rubbers. We have already seen (p. 241) that dimyrcene, as well as rubber, forms nitrosite C. Gutta-percha and normal artificial isoprene rubber also form nitrosites, so that the reaction is not at all specific. An abnormal rubber may nevertheless be distinguished by a change in the behavior of the nitrosite reaction. The same considerations hold true for the tetrabromide method, which does not involve a single chemical reaction, but proceeds with the evolution of more or less hydrogen halide. Unfortunately, the determination of the iodine number has not been used by Harries for differentiation of artificial rubbers, although it is very useful. L. Hock and G. Fromandi,[327] in working with artificial rubbers, determined the Kemp-Wijs iodine number for a "normal" isoprene rubber and for a sodium-isoprene rubber, and in both cases obtained a value for the iodine number which was only one-half the value for natural rubber. From this it follows that the isoprene rubber employed by them (the rubber was supplied by the Siemens Laboratory) was not "normal" according to our definition, but was extensively cyclicized. The cyclization processes which were systematically investigated by Staudinger (*see* p. 189) for natural rubber deserve the greatest attention in the preparation of artificial rubber. Cyclization cannot be avoided at higher polymerization temperatures or with certain catalysts. As cyclization proceeds beyond a certain degree, the resulting product differs more and more in its chemical properties from natural rubber.

Molecular weight determinations on artificial rubber were carried out by L. Hock and G. Fromandi, who, like Pummerer and Nielsen, worked with solutions of rubber in menthol (Rast method). The investigation was conducted only with quite concentrated solutions (one part rubber to seven parts menthol). The isoprene rubber referred to above as "normal" and the sodium-isoprene rubber gave values of 2,670 and 3,020, respectively, while a lower value (2,500) was obtained with natural rubber.

The above authors found that a two per cent solution of natural rubber in decalin was cyclicized by silent electric discharge. This change was evidenced by a gradual decrease in the iodine number and the viscosity. When four per cent solutions of the two above-mentioned artificial rubbers were subjected to the silent electric discharge, the iodine number and viscosity at first increased, thus manifesting an approach of these properties toward those of natural rubber. A subsequent decrease in the iodine number and viscosity indicated cyclization.

[327] G. Fromandi, *Kolloidchem. Beihefte*, **27**, 189 (1928).

In the following pages are presented the methods of preparation of a number of artificial rubbers made by Harries. These rubbers are described and classified according to their constitutions, insofar as these have been elucidated by him through ozone degradation. Literature references to some of the more recent polymerization procedures are included, the criticism of which has been omitted because of lack of perspective in the field.

Normal Types of Artificial Rubber

Normal Isoprene Rubber $(C_5H_8)_x$

1. *Polymerization of Isoprene with the Aid of Heat, according to Hofmann and Coutelle. (Repeated by Harries.)*[328] Pure isoprene is heated in sealed tubes containing 10cc. each. The time required for the contents of the tube to become viscous depends upon the temperature; e.g., 8 to 10 days at 100° to 110° C., 10 to 14 days at 85° C., 4 to 6 weeks at 60° C. After heating for a definite time the contents of the tubes are transferred to a fractionating flask. After distilling the unchanged isoprene, any terpene present is removed by diminishing the pressure to 10 mm. and heating the flask in an oil bath at 105° C. Polymerization at temperatures above 100° C., or at 95° C., produces variable yields. Below 100° C., the formation of terpenes is retarded.

The Badische Anilin-und Sodafabrik[329] has been granted patents which recommend the removal of the simpler products of polymerization by passing inert gases into the mixture. It was found[330] that the impurities which are tenaciously retained by the crude product could best be removed by treatment with steam *in vacuo*, during which the rubber swells and more readily gives up the enclosed particles. The temperature during this treatment must not exceed 100° C.

The rubber products obtained in the above method by the addition of other substances all show small differences, especially in vulcanization, from which it follows that products of varying molecular weight are present, or that they differ in their colloid chemical nature by being coarser or finer dispersions. Thus the rubber samples polymerized with acetic acid (Harries) differ in many respects from the rubber which is polymerized without the aid of additional substances.

Artificial rubber (prepared by the acetic acid process as well as by the auto-polymerization process) must be dried and preserved in an atmosphere of carbon dioxide, and must be protected from light, since the artificial rubber is readily attacked by the oxygen of the air (like purified natural rubber), and occasionally after a short time becomes friable and loses its elasticity. The varieties which have been polymerized at temperatures above 100° C. undergo these changes more readily than the more stable varieties prepared at lower temperatures. The susceptibility to oxygen is perhaps related to the cyclization which takes place at higher temperatures. Double bonds which occur in a ring are usually more reactive than those in an open chain and, in the case of cyclorubber, are probably more oxidizable.

2. *Polymerization with Heat and Acetic Acid.*[331] Isoprene is mixed with an equal volume of acetic acid and is heated on the water bath in a closed tube for about eight days at 100° C. The oil which separates from the color-

[328] Harries, "Untersuchungen ....," p. 171.
[329] Ger. Pat., 271,849, Class 39b (November 2, 1912); 272,349, Class 39b (December 4, 1912).
[330] Harries, "Untersuchungen ....," p. 171.
[331] Harries, *Ann.*, **383**, 190 (1911).

less solution is removed, and washed with alcohol. After standing for some time in a vacuum desiccator, the oil becomes solid and extensible. The yield is variable, but the reasons for this were not determined. Constant yields are not obtained with any given proportion of acetic acid, whether 2 drops or 30 cc. of acid are used with 20 cc. of isoprene. Variations in temperature from 95° to 120° C. produce little change. Even with the addition of only two drops of acetic acid, the liquid remains strongly acid for weeks. In this case the rubber does not separate, but must first be freed from unchanged isoprene which keeps it in solution. This is accomplished by distilling the isoprene at ordinary pressure. The rubber is then separated from lower polymerization products by distillation under reduced pressure. The purification is carried out by distilling the unchanged isoprene at atmospheric pressure, then diminishing the pressure to 10 mm. and heating in an oil bath at 105° C. until the oily distillate no longer passes over. The tough and at times very tacky residue is dissolved in ether, and is then precipitated with alcohol. A white substance, transparent and nearly colorless when dry, is produced. The properties of this product are very similar to those of reprecipitated natural rubber. If the temperature during polymerization is kept higher than 110° C., the polymer retains a brown color. The polymer at first is readily soluble in ether, benzene, chloroform, etc., but on standing for some time becomes more difficultly soluble and finally insoluble, and if then placed in contact with the solvent, it swells to a gelatinous mass.

A sample of isoprene rubber which was prepared by heating isoprene (Elberfelder process) for eight days in a closed tube at 105° C., in the absence of air, was purified once by reprecipitation. With this sample, Harries obtained analytical values which agreed very well with the formula $(C_5H_8)_x$. The isoprene used in the preparation was previously distilled over sodium. If less care is exercised in the preparation, a product is obtained which is not completely soluble in ether, and which, when redissolved in benzene, leaves a residue containing several per cent of oxygen. The formula of the benzene-soluble portion agrees fairly well with the formula $(C_5H_8)_x$. When the time of heating was extended to six weeks, Harries obtained an isoprene rubber of which one-third was insoluble in benzene, although the product behaved normally when ozonized.

In preparing the tetrabromide of normal isoprene rubber, it was found, as with natural rubber, that the purer the rubber, the greater is the evolution of hydrogen bromide. The compound $C_5H_8Br_2$ contains 70.14 per cent bromine. For the tetrabromide of natural rubber, when analyzed by the Carius method, Harries obtained values for the bromine content of 55.98 per cent and 68.16 per cent. With isoprene rubber, prepared under the same conditions, he obtained widely varying values of 60.75, 55.92, 65.38, 61.70 and 66.42 for the bromine content. The bromides of natural and of isoprene rubber behave similarly on heating. Decomposition of the bromides by heat therefore does not distinguish between the two types of rubber. Harries and Fonrobert[332] report analytical figures for the hydrochloride and hydrobromide of isoprene rubber which agree well with the theoretical values, and which far exceed in accuracy the values obtained with natural rubber by other investigators. In the case of the hydro-iodide, a difference seems to exist between natural and isoprene rubber, since the non-reprecipitated isoprene rubber gives a normal hydro-iodide $(C_5H_8HI)_x$, while after reprecipitation, a product is formed con-

[332] *Ber.*, **46**, 733 (1913).

taining only one-half the quantity of iodine $(C_{10}H_{16}HI)_x$.[333] This work should be repeated and supplemented by iodine values on the product obtained before and after reprecipitation. The hydrochloride of isoprene rubber, like that of natural rubber, gave on heating a regenerated rubber (iso-rubber) which behaved abnormally when subjected to ozone degradation. The degradation products no longer gave the pyrrole test. The nitrosite C from isoprene rubber [334] decomposed at a higher temperature than the nitrosite C obtained from natural rubber. The properties and composition of the nitrosite C of isoprene rubber are very much like those of the nitrosite of natural rubber, although the latter corresponds more nearly to the formula $(C_{10}H_{15}N_3O_7)_x$. A more detailed comparison has been given previously (*see* p. 241).

When destructively distilled under a pressure of 0.1 to 0.2 mm., both isoprene rubber and natural rubber behaved alike.[335] The ozonolysis of the fraction boiling between 220° and 260° C. gave no trace of levulinic aldehyde.

3. *Ozone Degradation of Artificial Isoprene Rubber.* According to Harries, artificial isoprene rubber behaves very much like natural rubber, with the exception that the presence of a more difficultly ozonizable portion is probably indicated by the fact that the ozone is consumed more slowly towards the end of the ozonization. An ozonide $(C_5H_8O_3)_x$ and an oxozonide $(C_5H_8O_4)_x$ can also be obtained from isoprene rubber. The products of ozone degradation are the same as are those obtained from natural rubber.

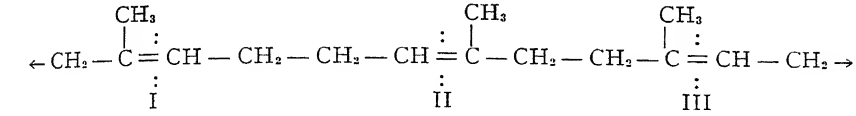
Analytically pure ozonide was obtained by Harries by evaporation of the chloroform or carbon tetrachloride solution *in vacuo* at 20° C., followed by several reprecipitations from ethyl acetate with petroleum ether. With a very pure starting material and prolonged drying *in vacuo,* this ozonide solidified to a glassy material. Heated on platinum foil, it exploded. In hot water, it first dissolved without decomposition, but after boiling the solution it decomposed. The rates of decomposition of this and other ozonides, as well as of the oxozonides of artificial rubbers, were determined by Harries, and the decomposition curves were compared with those of the corresponding derivatives of natural rubber and gutta-percha.[336] Artificial isoprene rubber is closely related to natural rubber and gutta-percha, while sodium-isoprene rubber differs considerably from natural rubber (*see* p. 216).

The yield of levulinic aldehyde and levulinic acid obtained in the ozonolysis of isoprene rubber is the same as that obtained from natural rubber. At times more aldehyde is obtained, at other times more acid. When 11.4 grams of ozonide were distilled with superheated steam, 3.3 grams of levulinic aldehyde were obtained in the distillate (isolated as 5.2 grams of methylphenyldihydro-pyridazine by means of phenylhydrazine, (*see* p. 212). After removing the levulinic aldehyde peroxide and resin (2.8 grams) by filtration, and evaporating the filtrate, a residue of 2.2 grams of levulinic acid remained. The oxygen evolved was calculated as 1.2 grams, giving a total loss of 1.9 grams. The decomposition of the oxozonide is analogous to that of the ozonide, but levulinic acid is produced in greater quantity. Samples of isoprene rubber prepared from isoprene obtained from widely differing sources and of varying degrees of purity were ozonized, and the results were always normal. The ozonide of artificial rubber, which was obtained by polymerization of isoprene with the aid of acetic acid, was slightly soluble in

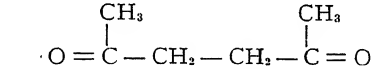
[333] Harries and Fonrobert, *loc. cit.*, also Harries, "Untersuchungen ....," p. 177.
[334] Harries, *Ann.*, **383**, 198 (1911).
[335] Harries, *Ann.*, **383**, 203 (1911).
[336] Harries, "Untersuchungen ....," p. 205, 222.

petroleum ether and yielded the same decomposition products as the ozonide of normal isoprene rubber, but in slightly different amounts.

Definite decomposition products other than those named above do not appear in the case of isoprene rubber. Steimmig,[337] however, found acetonylacetone among the decomposition products. This could be formed by the unsymmetrical polymerization of several isoprene groups, according to the following illustration:



in which the middle isoprene group is combined so that its methyl group is in the 3-position, while in the case of the first and third isoprene groups, it is in the 2-position. When degraded by ozone, II and III above would produce, instead of levulinic aldehyde, a different 1,4-dicarbonyl compound: namely, acetonyl acetone,



the typical decomposition product of methyl rubber, as we shall see later. In addition, succinic acid is produced by cleavage at I and II. Steimmig considered the formation of acetonyl acetone to be indicative of a structural difference between isoprene rubber and natural rubber. Harries showed, however, by means of very carefully conducted experiments, that the isoprene employed by Steimmig was not entirely pure, and that in the polymerization of the purest isoprene, only traces of acetonyl acetone were formed.[338] From 68.3 grams of ozonide, he obtained only 0.16 gram of acetonyl acetone and 0.6 gram of succinic acid. This controversy is very instructive. Impurities in the isoprene can also be polymerized and thus yield impurities in the final product. They can also interfere with the usual polymerization process, and to some extent cause the formation of other polymers from isoprene.

By heating isoprene at higher temperatures, dipentene, a cyclic terpene of the formula $C_{10}H_{16}$, is produced as a by-product.[339] From freshly prepared rubber obtained in the polymerization of isoprene with heat, Harries could identify only a small quantity of the by-product, dipentene. However, he observed an oil having the odor of myrcene and a boiling point of 63° to 65° C. at 14 mm. pressure, which may possibly be an open chain terpene, $C_{10}H_{16}$.

4. *Polymerization without Heat.* After the discovery of the process for polymerizing isoprene with the aid of heat, attention was again directed to the much discussed statement of Bouchardat and Tilden that isoprene forms rubber on standing in a closed flask at room temperature. Harries demonstrated that larger quantities of pure isoprene remained unchanged for several years. On the other hand, Pickles,[340] in 1910, using Harries' method for the identification of rubber (tetrabromide, nitrosite C), showed that a sample of isoprene, preserved for three years, contained a certain amount of rubber. In 1916, Harries obtained more of such a product which was obtained without the aid of heat. A flask containing isoprene which had been stored for some time became unsealed and started to leak around the glass

[337] *Ber.*, **47**, 350, 852 (1914).
[338] *Ber.*, **47**, 573, 1999 (1914); **48**, 863 (1915).
[339] For the structural formula, see p. 185.
[340] *J. Chem. Soc.*, **97**, 1085 (1910).

stopper. The isoprene had not completely evaporated, but had formed a soft, colorless, rubber-like film around the stopper and on the flask. Probably the oxygen of the air (perhaps other catalysts) is necessary for the polymerization without heat, since oxidation products of rubber, limonene, and other hydrocarbons have already been proposed as catalysts for the polymerization of isoprene with heat. Polymerization under the above conditions is a method of formation and not a practical process for the preparation of the polymer. It seems very probable, however, that with suitable catalysts, isoprene rubber can be manufactured without heat, and that the polymerizate may possess many advantages. The danger of cyclization under these conditions is less than when heat is used to polymerize the isoprene.

Harries was able repeatedly to obtain and investigate the rubber-like product formed by polymerization without heat. It differs distinctly from the polymer obtained with the aid of heat, since it remains soft and tacky and possesses no nerve. It is dissolved more readily by the usual rubber solvents than is the polymer obtained with the aid of heat, and remains soft and tacky after reprecipitation from benzene by alcohol. On heating *in vacuo* at 100° C., it liberates small quantities of terpenes. A yellow, transparent mass remains, which has little resistance to tear and produces an ozonide, which, on decomposition, yields essentially levulinic aldehyde and levulinic acid, the latter, however, in "abnormally large" quantities (8 times the amount of aldehyde). The high rate of decomposition of the ozonide is also abnormal; but from its chemical properties, the product must be classed as rubber (from the ozone degradation, and the formation of the nitrosite and the tetrabromide). The mechanical properties and the solubility of this polymer vary considerably from those of isoprene rubber produced with the aid of heat and from those of natural rubber. The polymer obtained by Kondakoff from dimethylbutadiene without heat differs chemically even more from the isoprene polymer obtained with heat.

5. *Sodium-Carbon Dioxide-Isoprene Rubber.* The sodium-carbon dioxide rubber prepared by A. Holt [341] of the Badische Company, can be regarded as a rubber with a particularly high molecular weight. It is possible that the slight solubility of the polymer is related to the uniform, fiber-like, parallel arrangement of the molecules, which are formed on the sodium wire.

This compound must also be classed among the normal types of rubber. In an address delivered before the Heidelberg Chemical Society, Holt [342] reported that it is produced by prolonged shaking of isoprene with sodium wire in a completely dry atmosphere of carbon dioxide. It was found [343] necessary to exclude all traces of moisture, because when small quantities of water are present, another product is formed, which possesses more nearly the properties of the so-called "abnormal" sodium-isoprene rubber (*see* p. 264). To prepare the sodium-carbon dioxide-isoprene rubber, a tube previously drawn out to capillary size is filled with 20 cc. of isoprene previously distilled over sodium. Three to four pieces of sodium wire about 40 cm. long are added, and a dry stream of carbon dioxide is passed through the tube for about three minutes, after which the capillary is quickly sealed. The tube is then heated on the water bath at 60° C. for a period of two to three weeks. The sodium becomes covered with a black porous worm-like mass, while the isoprene completely disappears. The reaction takes place almost quantitatively. To purify the product, the rubber is suspended in

[341] *Chem.-Ztg.*, **38**, 188 (1914).
[342] *Chem.-Ztg.*, **38**, 199 (1914); see also Steimmig, *Ber.*, **47**, 350 (1914).
[343] Harries, "Untersuchungen ....," p. 190.

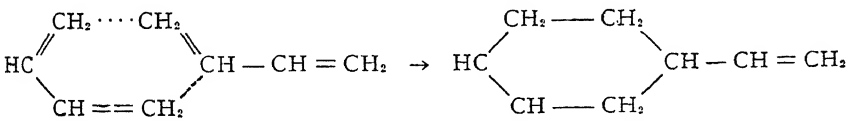
dilute alcohol, in which the sodium dissolves, and from which the product is obtained as a beautiful white solid. This product is insoluble in all solvents and is similar to the white product which is formed when isoprene is polymerized by ultra-violet light. It must be carefully preserved with exclusion of air, else it is converted in a short time to a soft, tough, brown mass which is soluble in certain solvents. This sodium-carbon dioxide rubber therefore behaves similarly to the white polymer obtained by Kondakoff in the polymerization of dimethylbutadiene without heat (*see* p. 262).

Sodium-carbon dioxide-isoprene rubber is related to normal isoprene rubber, since, according to Holt,[344] the decomposition of the ozonide with water yields the same products which are obtained by the ozonolysis of normal isoprene rubber. The sodium-carbon dioxide-isoprene rubber is therefore also related to normal isoprene rubber. No further data on sodium-carbon dioxide-isoprene rubber have been published to date.

Normal Butadiene Rubber

According to Harries,[345] the polymerization of butadiene is less easily accomplished than the polymerization of isoprene. After heating butadiene for 10 days at 100° to 103° C., alone or with acetic acid, most of the hydrocarbon remains unchanged. After heating for ten days at 110° to 120° C., a reaction has taken place. At 105° C. the polymerization requires about four weeks. Below 100° C. several months are required, but under these conditions the best product is obtained in the form of a white, transparent, very tough substance. The polymerization is best conducted without the addition of acetic acid.

The butadiene rubber prepared at 110° to 120° C. was first heated *in vacuo* at 100° to 110° C. by Harries to remove the butadiene-terpene which was also formed during the polymerization. This terpene is formed from two molecules of butadiene according to the following scheme:



Ozonization of the terpene yielded butanetricarboxylic acid.[346] The terpene had the following physical properties: B.p. 36° C. at 23 mm.; $d_4^{16} = 0.8523$; $n_D^{16} = 1.46768$. The composition corresponded to the formula C_8H_{12}.

The residue of butadiene rubber which remained after vacuum distillation was very difficultly soluble in the usual rubber solvents. After extraction with boiling benzene it was analyzed. The composition corresponded to the formula $(C_4H_6)_x$ except for the fact that the carbon value was 2 per cent low, which is not surprising in view of the slight purification possible. Solution in carbon tetrachloride (80 to 100 cc. for 1 gram of rubber) was finally accomplished by heating and shaking in a sealed tube at 80° C. for twelve hours in an oven. If the butadiene is polymerized at lower temperatures, the resulting rubber is somewhat more soluble.

The tetrabromide of butadiene rubber does not give constant analytical values (*see* the values for isoprene rubber, p. 255). The nitrosite corresponds

[344] *Loc. cit.*
[345] Harries, *Ann.*, **383**, 206 (1911).
[346] F. Hofmann and L. Tank, *Z. angew. Chem.*, **25**, 1465 (1912).

to the formula $(C_5H_{12}N_2O_6)$. The ozonization in carbon tetrachloride produced only a small quantity of the ozonide (50%), which was precipitated as a gelatinous mass. The solution was evidently not analyzed. The ozonide is insoluble and explosive, and is difficult to decompose with boiling water. The decomposition of the ozonide is accompanied by the evolution of a gas. No hydrogen peroxide could be found among the decomposition products; but considerable quantities of succinic dialdehyde, $O=\overset{H}{\overset{|}{C}}-CH_2-CH_2-\overset{H}{\overset{|}{C}}=O$, were detected by the pyrrole test. Succinic acid was also detected among the products. Two grams of the phenylhydrazone of succinic dialdehyde, corresponding to about 0.6 gram of the aldehyde, were obtained from 9.5 g. of the ozonide. An attempt to determine the amount of succinic acid formed was unsuccessful. The two decomposition products point to a normal polymerization of butadiene according to the following formula, with double bonds recurring after each fourth carbon atom.

$$\underset{\text{I}}{CH_2-CH=CH-CH_2}-CH_2-\underset{\text{II}}{CH=CH}-CH_2-CH_2-\underset{\text{III}}{CH=CH}-CH_2$$

The decomposition by ozone at the double bonds I, II, and III in this case results in fragments with four carbon atoms, while in the similar decomposition of isoprene rubber, products containing five carbon atoms are formed, and in the decomposition of dimethylbutadiene rubber, substances with six carbon atoms are formed. From a historical standpoint, the ozonide is interesting because of its similarity in appearance and rate of decomposition to the ozonide of cyclo-octadiene. This similarity led Harries [347] to conclude at the time of his experiments that the eight-membered ring formula for rubber had been proved. (*See* p. 215.)

Normal Dimethylbutadiene Rubber

1. *Polymerization with Heat (Commercial Methyl Rubber).* By far the best process for the polymerization of dimethylbutadiene with heat is that of Hofmann and Coutelle (previously described), which was utilized commercially by Farbenfabriken vorm. Friedrich Bayer & Company during the war. The polymerization of dimethylbutadiene with acetic acid gives a tacky, yellow product of little value. The polymerization of dimethylbutadiene (at least with the aid of heat) takes place more sluggishly than the polymerization of isoprene, according to Harries. The polymer obtained from dimethylbutadiene without the aid of heat (Kondakoff) and its yellow, resinous transformation product are readily produced; but the ozone degradation of this polymer does not give the usual results (see p. 262). In order to characterize methyl rubber, Harries used a polymer which was obtained by heating dimethylbutadiene for a period of 23 days at 100° C. From 50 grams of the starting material, he obtained 16 grams of rubber and very little of terpene compounds. The remainder was unchanged dimethylbutadiene. The rubber, reprecipitated from ether solution with alcohol, was slightly colored, transparent, and somewhat more soluble than isoprene rubber. The bromide as well as the hydrohalide derivatives could be prepared in analytically pure form, one molecule of bromine or one molecule of the halogen acid (even HI) being taken up by each C_6H_{10} group. The

[347] *Ber.*, **41**, 674 (1908).

nitrosite had the formula $C_{12}H_{19}N_3O_7$, corresponding to the nitrosite obtained from isoprene rubber.

Ozonide. A solution of 7.5 grams of rubber in 100 cc. of carbon tetrachloride was ozonized until the solution no longer decolorized bromine (nine hours). Eleven grams of the crude diozonide were obtained by evaporating the solution *in vacuo* (theoretical yield, 11.8 grams). Reprecipitation from ethyl acetate with petroleum ether demonstrated that a readily soluble portion (decomposition product?) and a difficultly soluble portion were present. The difficultly soluble portion of the ozonide remained light colored when decomposed by heating with glacial acetic acid on the water bath, while the readily soluble portion turned brown after the same treatment. The decomposition of the ozonide with boiling water was carried out quantitatively, and the rate of decomposition was determined. The principal product, which was formed in about 80 per cent yield, was acetonyl acetone of the formula :[348]

$$O=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=O$$

If the dimethylbutadiene polymerizes as would be expected according to Thiele's theory—by 1,4-addition at the ends of the conjugated system $(A.....)$—

$$A\cdots CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2\cdots \quad \cdots CH_2-\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2\cdots \quad \cdots CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2\cdots$$

the following structural formula B results:

$$B\longleftarrow CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_2\longrightarrow$$

normal dimethylbutadiene rubber

in which the double bonds lie between the carbon atoms having methyl groups attached. According to this formula, acetonyl acetone, a diketone, should be formed on ozonolysis, instead of a keto-aldehyde, which could be further oxidized to an acid. The highest yield of a definite decomposition product ever recorded in the ozonolysis of any rubber, was obtained in this case (80%). The formation of acetonyl acetone shows that in the polymerization, the double bonds have actually migrated, in accordance with Thiele's hypothesis, to the central position, between the carbon atoms carrying methyl groups. In the cases of isoprene rubber and natural rubber, the positions of the double bonds in the molecule cannot be determined, but their locations are deduced from experiments such as the above, and from theoretical conclusions in other branches of organic chemistry. The acetonyl acetone is quantitatively determined by forming the beautifully crystalline diphenylhydrazone having a melting point of 190° C.

Harries states that the crude acetonyl acetone obtained from methyl rubber always reduces Fehling's solution. It can be concluded that an aldehyde (probably a keto-aldehyde), which has a boiling point close to that of the acetonyl acetone is present. The amount of this by-product, which is apparently only formed in small quantities, was not determined quantitatively, nor was it isolated or identified. It results from the migration of a double bond in B or from an abnormal reaction of dimethylbutadiene during polymerization.

[348] The oxozonide behaves in the same way when decomposed.

2. *Polymerization without Heat.* The white, insoluble product obtained by Kondakoff in 1901 from the polymerization of dimethylbutadiene in the cold cannot, according to its properties, be classed as rubber. It is discussed at this point, with the normal types of rubber, because on ozonolysis, according to Harries, it always yields 30 to 50 per cent of acetonyl acetone. Its chemical structure is therefore to a certain extent analogous to the product obtained by polymerization with heat, which yields 80 per cent of acetonyl acetone on ozonolysis. This relationship is further shown by the ease with which ozone attacks the product of the polymerization without heat, forming the oxozonide, if the concentration of ozone in the gas is not too dilute. The rates of decomposition of the ozonides of the polymers obtained with and without heat are quite different, the latter ozonide being more difficult to decompose. In this respect, the dimethylbutadiene polymer obtained without heat is different from the corresponding polymer of isoprene (*see* p. 258).

The transformation of Kondakoff's product into a plastic mass, which results from further heating to 80° to 100° C., according to a patent of Farbenfabriken vorm. Friedrich Bayer & Co.,[349] does not alter the product so much that its constitution becomes similar to the structure of dimethylbutadiene polymerized with heat. Harries was unable to obtain more than 50 per cent of acetonyl acetone by ozonolysis of the transformed product.[350]

3. *The yellow soluble resin obtained from the white product resulting from polymerization without heat.* The polymer obtained without the aid of heat is transformed after standing for several hours in the air to a yellow mass which has sintered together and which is now soluble in the usual solvents. Harries ozonized this resin and obtained 35 per cent of the theoretical quantity of acetonyl acetone.

The ozonolysis of the substances discussed above, always yields other products which have not been identified. Among these there is an aldehyde which is possibly formed in larger quantities than in the ozonolysis of the polymer obtained with the aid of heat.

Normal Piperylene Rubber[351] *(1-Methylbutadiene Rubber)*

Piperylene (*see* p. 251) was polymerized at 105° to 110° C. in a sealed tube for 14 days. The unchanged piperylene was distilled. The terpene formed as a by-product was removed *in vacuo* at 50° to 70° C. The product was then dissolved in ether, precipitated with alcohol, and dried over sulfuric acid *in vacuo*. The resulting rubber was fairly pure, of good quality, and similar to isoprene rubber. It is impossible definitely to differentiate piperylene rubber from isoprene rubber by preparing its nitrosite C or tetrabromide derivatives. It is easier to distinguish the piperylene rubber by preparing the ozonide, which is only converted to the oxozonide with the greatest difficulty and by the use of ozonized oxygen containing a high concentration of ozone. In the decomposition of the oxozonide, levulinic aldehyde is not formed in sufficient quantity to be detected as the pyridazine derivative by means of phenylhydrazine. The aqueous forefraction from the distillation of the solution containing the ozone decomposition products, as well as certain oily fractions, gave the pyrrole test and reduced cold Fehling's solution. Harries and Schönberg could not detect methyl succinic aldehyde, although it is probably formed.

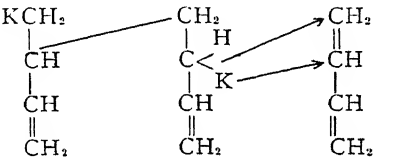
$$\begin{array}{l} CH_3-CH-CH=O \\ \quad\quad | \\ \quad CH_2-CH=O \end{array}$$

[349] Ger. Pat., 254,668, Class 39b, 1.
[350] Harries, "Untersuchungen ....," p. 200.
[351] Harries and Schönberg, *Ann.*, **395**, 243 (1913).

This aldehyde must be produced, if piperylene rubber is formed by the normal polymerization of piperylene by 1,4-addition. The rate of decomposition of the ozonide is decidedly lower than that of the ozonide of isoprene rubber.

Abnormal Types of Artificial Rubber (Sodium Rubbers)

According to K. Ziegler and H. Bähr,[352] the mechanism of the polymerization by means of sodium or potassium can be explained, by assuming that through addition of potassium to butadiene, a 1,2-dipotassium derivative is first formed, which then adds to a second butadiene molecule in the 1,2-position. The new substance then adds a third butadiene molecule in the following manner:



According to this scheme, a long chain containing vinyl groups as substituents is finally formed. This explains the variable results obtained in the ozonolysis of sodium rubber.

Sodium-butadiene Rubber [352a]

The polymerization of butadiene by means of sodium (*see* p. 242) is carried out as follows: Sodium wire, together with the hydrocarbon, is placed in a sealed tube. The butadiene is polymerized to a solid mass in a short time when the tube is heated on the water bath at 35° to 40° C. At room temperature the process requires a longer time. To obtain the product, the tube, in which no pressure exists, is opened, and the reaction product is washed with alcohol to remove the sodium. The rubber assumes a light yellow color after washing. In the freshly prepared condition, the sodium-butadiene rubber is readily soluble in ether, chloroform, and benzene. On standing, especially if milled (slight auto-oxidation) the rubber becomes less and less soluble in the above solvents. The rubber swells readily in the usual organic solvents, and produces very viscous solutions on standing for some time in contact with the solvents. The analysis indicates the formula $(C_4H_6)_x$. The dibromide contains 68.7 per cent of bromine, instead of 74.7 per cent, which is the calculated amount for the formula $C_4H_6Br_2$. The calculated bromine content for a monobromide corresponding to the formula $(C_4H_6Br)_x$, is 60 per cent. The nitrosite of sodium-butadiene rubber behaves differently from those previously described. It forms as a yellow precipitate, but does not become soluble in ethyl acetate or acetone after standing in contact with nitrous acid for days. It varies considerably in composition, and has a nitrogen content of 12 to 13 per cent.

Matthews and Strange polymerized butadiene in the vapor phase with sodium wire as catalyst. Sodium alkyls alone or in a mixture with zinc alkyls,[353] as well as amalgams and colloidally dispersed metals (Hg, Ag,

[352] *Ber.*, **61**, 253 (1928).
[352a] Harries, *Ann.*, **383**, 213 (1911).
[353] Badische Anilin- und Sodafabrik, Brit. Pat., 5,667 (1912).

Pt)[354] were also suggested as catalysts in the place of the alkali metals. Finally, sodium rubber itself and sodium-carbon dioxide rubber were proposed as catalysts.[355]

Ozonide. When a chloroform solution of sodium-butadiene rubber is treated with ozonized oxygen containing 6 to 7 per cent of ozone, an oily ozonide (remaining in solution) is obtained. With a concentration of 12 to 14 per cent of ozone, a solid, very explosive ozonide is precipitated, which must be washed and dried with great care. If the ozonide is allowed to stand under ether for a long time, there is less danger of explosion. In the formation of either of these two ozonides, the ozone absorption required an abnormally long time. The ozonization of two grams of the rubber required 10 hours when the less concentrated ozone gas was used, and 3 hours with the higher concentration of ozone. Ethyl acetate or glacial acetic acid dissolves the oily, but not the solid, ozonide. The composition of the oily ozonide corresponds approximately to the usual formula $(C_4H_6O_3)_x$, while the solid ozonide shows the surprisingly high carbon content of 50.5 per cent. ($C_4H_6O_3$ contains 47 per cent carbon, while $C_8H_{12}O_3$ contains 61.5 per cent carbon.) Some of the double bonds of the solid ozonide have not been attacked, despite the fact that a high concentration of ozone was used, from which Harries concluded that a conjugated system of double bonds is present in the original rubber. Such a system of double bonds in general reacts more slowly with ozone, and readily forms mono-ozonides.[356] On drying, the oily ozonide passes into a slightly explosive, porous, white, solid mass which on hydrolysis gives only a faint pyrrole test, but gives a test for hydrogen peroxide. The rate of decomposition is abnormally high and can hardly be measured. Among the decomposition products, only glyoxal was identified by means of phenylhydrazine and semicarbazide. The formation of glyoxal also points to a conjugated system of double bonds.

Sodium-isoprene Rubber $(C_5H_8)_x$

Isoprene is polymerized by sodium with greater difficulty than butadiene and must be very pure in order to allow polymerization.* An almost theoretical yield of solid rubber is obtained by the polymerization of pure isoprene in a sealed tube at 60° C. within a period of 50 hours. Harries conducted his investigation with a sample of less pure isoprene obtained from carvene. He allowed 0.2 to 0.5 gram of fine sodium wire (40 to 80 cm. in length) to react with 10 grams of isoprene at 60° C. for a period of four to five days. An analytically pure product is obtained by dissolving the product in ether and precipitating it with alcohol. Sodium-isoprene rubber is dissolved more readily than normal isoprene rubber by the usual solvents. Its physical-mechanical properties are very similar to those of normal isoprene rubber. The sodium-isoprene rubber on pulling stretches out into rather broad bands while the normal isoprene rubber when pulled assumes a stringy form. The two rubbers differ chemically in various ways. The greatest

[354] Farbenfabriken vorm. Fr. Bayer & Co., Ger. Pat., 304,959 (1918).

[355] Badische Anilin- und Sodafabrik, Ger. Pat., 294,816 (1917).

[356] Harries, *Ann.*, **374**, 304 (1910).

* Translator's Note. Midgely and Henne [*J. Am. Chem. Soc.*, **51**, 1294 (1929)] have recently polymerized isoprene under conditions which normally produce "sodium rubber." They succeeded in stabilizing the dimer of isoprene and isolating the partially hydrogenated dimer. Pure isoprene was treated with sodium and alcohol. The reaction resulted in a mixture of three isomeric dimethyl octadienes, namely 2,6-, 2,7-, and 3,6-dimethyl-2,6-octadienes. The formation of these compounds by polymerization and reduction of isoprene indicates that the mechanism of the polymerization of isoprene by means of sodium involves the joining of a large number of isoprene groups by linkage of the 1,1-, the 1,4-, or the 4,4-carbon atoms with formation of long chain molecules.

difference is shown in their behavior toward ozone, while the dibromide of sodium-isoprene rubber is very little different from the corresponding normal rubber derivative. The former contains 68 per cent of bromine (the calculated value for $C_5H_8Br_2$ is 70.1 per cent). The nitrosite of sodium-isoprene rubber is not a uniform substance. The greater portion of this nitrosite is difficultly soluble in ethyl acetate but more readily soluble in acetone, while the remainder is insoluble in acetone. The main fraction of the nitrosite is yellowish-white, becomes light brown when heated to 170° C., dark brown at 180° C., and undergoes no further change when heated to 260° C. The composition of the nitrosite differs considerably from that of nitrosite C and varies widely from that expressed by the formula $(C_{10}H_{16}N_2O_5)_x$.

Ozonide. Sodium-isoprene rubber always contains some admixed normal isoprene rubber, because the polymerizing action of sodium at 60° C. (the usual temperature of polymerization) is slow, and at this temperature some isoprene rubber is produced by the polymerizing action of heat. The presence of normal isoprene rubber can be observed in a study of the ozone decomposition products of sodium rubber (faint pyrrole test, isolation of small quantities of levulinic aldehyde). When 5 grams of sodium rubber dissolved in 60 cc. of carbon tetrachloride are ozonized for 10 hours (a long time is required) with oxygen containing 12 to 14 per cent of ozone, the main portion of the ozonide is obtained as a white, gelatinous substance. When filtered and washed with ether, it becomes solid and crumbly. It is purified by dissolving in ethyl acetate (which does not dissolve it entirely), and precipitating with ligroin. The ozonide contains 3 per cent more carbon than the value (51.71 per cent) required by the formula $(C_5H_8O_3)_x$, and therefore contains unsaturated double bonds. An ozonide which agreed very well with the above formula was obtained by the action on sodium rubber of a current of air containing 6 to 7 per cent of ozone. An oxozonide is formed with difficulty by treatment with ozone for several days.

A typical curve is obtained for the rate of decomposition of the ozonide. During the decomposition a part of the ozonide remains insoluble in the form of a yellow resin. The solution contains, in addition to formic acid and small quantities of a volatile aldehyde, at least two acids of high molecular weight which, because of their reducing properties, are designated as aldehyde- and/or ketone-acids.[357] Harries[358] concludes from these results that the sodium rubbers consist of large, complex molecules, suggestive of the resins.* The value obtained for bromine on analysis of the dibromide seems to preclude extensive cyclization in the sodium rubber molecule. It will be necessary, however, to reinvestigate the number of double bonds in the molecule of sodium rubber, with a satisfactory method for the determination of the iodine number (*see* p. 253). It is very probable that partially or sometimes very extensively cyclicized products are present in the sodium rubbers and in the resins. One mol of hydrogen chloride is added to sodium rubber, forming a hydrochloride of the formula $(C_5H_8HCl)_x$, while only one-half mol of hydrogen bromide or hydrogen iodide is added per C_5H_8 group, forming rub-

[357] The analytical figures for a syrupy and an amorphous acid corresponded approximately to the formula $C_{16}H_{20}O_{10}$ and $C_{25}H_{36}O_{10}$, respectively. Harries, *Ann.*, **406**, 180 (1914).

[358] Harries, "Untersuchungen . . . . ," p. 219.

* Translator's Note. T. Midgley, A. L. Henne and A. F. Shepard [*J. Am. Chem. Soc.*, **54**, 381 (1932)] have compared the products obtained from the pyrolysis of sodium rubber with those obtained from natural rubber. The composition of the products in the two cases leads to the conclusion that sodium rubber is isomeric with natural rubber in the positioning of the methyl groups and that the double bond of sodium rubber differs from the true ethylenic bond of natural rubber.

ber hydrohalides corresponding approximately to the formula $(C_{10}H_{16}.HX)_x$. By removal of hydrogen chloride from the hydrochloride, Harries succeeded in obtaining a regenerated rubber which was not ozonized.

Sodium-dimethylbutadiene Rubber $(C_6H_{10})_x$

The method of preparation of sodium-dimethylbutadiene rubber is the same as that of sodium-isoprene rubber (heating 10 to 12 days at 60° C.). The product is taken up in ether, in which part of the rubber remains undissolved as a white solid mass. The rubber is then precipitated from the ether solution with alcohol. The soluble portion is very different from isoprene rubber in appearance, and resembles gutta-percha. In its reactions (nitrosite and dibromide) the sodium-dimethylbutadiene rubber behaves analogously to isoprene rubber, even to the extent of always forming some acetonyl acetone on ozonolysis. The acetonyl acetone results from the rubber which has been produced by normal polymerization. The ozonide is a thick oil which, on decomposition, gives a test for hydrogen peroxide. Most of the decomposition products of the ozonide have not been identified.

Sodium-piperylene rubber was also prepared by Harries, who employed the same method which was used for the preparation of sodium-isoprene rubber. The sodium-piperylene rubber became only slightly elastic and remained tacky on long standing. It has not been further investigated.

Other Polymerization Methods

The following additional polymerization methods have been proposed:

Method for the preparation of diolefins and their polymerization products. Plauson's Research Institute, Hamburg, Ger. Pat., 338,030, Class 12-o.[359]

Mixtures of unsaturated hydrocarbons of the ethylene and acetylene series are heated under pressure in the presence of contact catalysts such as oxides and hydroxides of the alkali and alkaline earth metals (the gaseous mixture is diluted with inert gases and vapors). It is claimed that 1,4-diolefins and their polymerization products are formed.

Process for the preparation of rubber or its homologs from isoprene or its homologs and analogs. H. v. Euler, Stockholm, Ger. Pat., 301,088, Class 39b.[360]

Isoprene is heated with alkyl esters of inorganic acids, e.g. amyl nitrite or amyl halides.

Process for the preparation of rubber-like substances. H. Otto Traun, Hamburg, Ger. Pat., 329,593, Class 39b.[361]

1,4-dienes are polymerized at 50 to 600 atmospheres pressure at normal temperature, with or without the addition of polymerization catalysts.

Process for the preparation of products similar to rubber. Badische Anilin- und Sodafabrik, Ger. Pat., 307,341, Class 39b.[362]

1,4-dienes are polymerized with the addition of sodium-carbon dioxide rubber, which has been washed free from alkali.

Process for the preparation of vulcanizable substances related to rubber. Plauson's Research Institute, Hamburg, Ger. Pat., 371,710, Class 39b.[363]

Acrolein-alkyl or arylamines (for example, acrolein methylamine) are added to 1,4-butadienes before polymerization. Polymers which vulcanize well are obtained.

[359] *Friedländer*, "Fortschritte ...," **13**, 633.
[360] *Friedländer*, "Fortschritte ...," **13**, 636.
[361] *Friedländer*, "Fortschritte ...," **13**, 637.
[362] *Friedländer*, "Fortschritte ...," **13**, 639.
[363] *Friedländer*, "Fortschritte ...," **14**, 688.

Preparation of plastic masses from styrene. Naugatuck Chemical Co., U. S. Pat., 161,637, Jan. 29, 1925.

Rubber, gutta-percha, balata, or similar rubber resins are dissolved in styrene to make 5 per cent solutions, and the mixture is polymerized by heating to 135° to 140° C. The solid masses are characterized by high flexibility and good mechanical workability.

Rubber-like masses. Charles Albert Houques-Fourcade, French Pat., 622,896, October 9, 1926.

Sea algae are dissolved in 5 to 10 per cent soda solution. After removing the insoluble matter, the solution is heated with sulfur at 110° C., or is treated with sulfur monochloride, or with sulfur dioxide and hydrogen sulfide.

Removal of liquid polymerization products from synthetic rubber by means of activated charcoal or other porous adsorption agents. I. G. Farbenindustrie, Brit. Pat., 267,808, Sept. 3, 1926.

Preparation of artificial rubber from the products obtained by the hydrogenation under pressure of petroleum, coal or coal-like substances. Polymerization of the pressure hydrogenation products of petroleum, coal, or coal-like substances, or the extraction, distillation or transformation products of these substances to high molecular weight rubber hydrocarbons. The above substances may also be dehydrogenated or decomposed to unsaturated compounds, which can then be polymerized to high molecular weight rubber hydrocarbons. I. G. Farbenindustrie, Brit. Pat., 234,857, May 23, 1927.

Artificial rubber. I. G. Farbenindustrie, Brit. Pat., 283,840, January 16, 1928.

Suitable hydrocarbons, such as butadiene, isoprene or dimethylbutadiene, are emulsified in soap or protein solutions, and are polymerized in the presence of oxygen or substances which evolve oxygen.

Artificial rubber. I. G. Farbenindustrie, Brit. Pat., 283,841, January 16, 1928.

Hydrocarbon compounds which are suitable for the preparation of artificial rubber are polymerized by alkali metals in the presence of organic hydroxy compounds, such as starch, cellulose or cellulose ethers, in an atmosphere of hydrogen, nitrogen or carbon dioxide.

Synthetic rubber. I. G. Farbenindustrie, Brit. Pat., 294,661, July 27, 1928.

The polymerization of butadiene, isoprene, dimethylbutadiene, etc., with oxygen or substances which evolve oxygen is carried out in the presence of a metal salt (Co, Pb, Mn, Cr, Ni, Ag) of an inorganic or organic acid, if desired in the presence of a protective colloid (water solutions of blood albumen, casein, or tetrahydronaphthalene sulfonic acid).

Synthetic rubber. I. G. Farbenindustrie, Brit. Pat., 294,963, August 1, 1928.

Isoprene or similar hydrocarbons are polymerized by shaking at 60° C., in the presence of compounds which exert a hydrotropic effect, such as casein and potassium cinnamate, blood albumen and the sodium salt of tetrahydronaphthalene sulfonic acid, the magnesium salt of isobutyl naphthalene sulfonic acid or protein and sodium stearate.

Preparation of synthetic rubber. Goodyear Tire and Rubber Co., Brit. Pat., 297,050, May 31, 1928.

Unsaturated hydrocarbons are emulsified in water solutions of ammonium or potassium oleate with the addition of a 2 per cent casein or protein solution, and the mixtures are heated in closed vessels for six months at 50° to 70° C. The reaction product is coagulated with alcohol.

Preparation of artificial rubber. I. G. Farbenindustrie, Brit. Pat., 646,704, January 4, 1928.

Emulsions of butadiene hydrocarbons, their homologs or analogs, in water solutions of sodium oleate, of sodium isobutylsulfonate or of turkey red oil and Na_3PO_4, are polymerized by heat, light of short wave length, or other polymerizing agents (acrylic acid, or condensation products of acrolein). Artificial latex is obtained.

Synthetic rubber. I. G. Farbenindustrie, Brit. Pat., 301,515, December 1, 1928.

Butadiene or its homologs or analogs are polymerized in water solutions of bile acids, such as desoxycholic acid, apocholic acid or animal bile. Coagulable emulsions similar to latex are obtained.

Preparation of synthetic rubber. I. G. Farbenindustrie, Brit. Pat., 286,272, March 1, 1928.

Colloidal water solutions or suspensions of isoprene, etc., are polymerized with electrolytes in presence of oxygen or in an atmosphere of inert gas. The hydrocarbon is mixed with water solutions of protein, glue, casein, alkali oleate, or saponin, and electrolytes are added, such as calcium caseinate, sodium sulfate, potassium iodide, sodium chloride, acetic acid, or phosphoric acid.

Artificial rubber. I. G. Farbenindustrie, Brit. Pat., 302,733, December 20, 1928.

Rubber masses are obtained from synthetic rubber by adding various highly polymerized products (differing in the degree of polymerization) of the same hydrocarbon of the butadiene series.

It has been possible to cite only a few of the patents issued during the last few years. These patents will serve to show the renewed interest in synthetic rubber and to call attention to the patent information in Friedländer's "Fortschritte der Teerfarbenfabrikation." Naturally it was not possible to discuss some 500 German patents in which the German discoveries in this field are presented, and which served as the incentive for the discovery and use of vulcanization accelerators (*see* p. 309). In contrast to the other methods of preparing synthetic rubber, it is necessary again to point out that it was Fritz Hofmann [364] who, undaunted by the failures of eminent colleagues in this field and disregarding the then accepted eight-membered ring hypothesis of Harries, attacked the problem of the technical preparation of synthetic rubber from isoprene and other dienes, at the Farbenfabriken vorm. Friedr. Bayer & Company. Through consistent investigational work with a number of ex-

[364] *Cf.* also Fr. Hofmann's controversy with Harries; communications from the Fritz von Friedländer — Fuld Kohlenforschungsinstitut in Breslau, "Zur Geschichte des synthetischen Kautschuks," **1**, 70 (1920); also *Z. angew. Chem.*, **25**, 1462, 1858 (1913), where the alleged priority of the Heinemann patent is disputed.

Harries did not obtain a German patent on his acetic acid polymerization process, because it was anticipated by older applications (pertaining to acid catalysts) of Farbenfabriken vorm. Friedrich Bayer & Co.

ceptional co-workers, he proceeded a long way in solving the problem. Among these co-workers, the following should be mentioned: Merling, Coutelle, Meisenburg, Delbrück, Jonas, Tschunkur, Köhler, Bögemann, Schmidt, Tank, Pfeffer, Gottlob, Zieser, Chrzcescinski and Michael. The entire work would have been impossible without the active and far-sighted support of C. Duisberg. Not so many years ago, the syntheses of alizarin and indigo (which stand as lasting triumphs to organic chemistry) were accomplished by German chemists. It is to be hoped that the old and new forces which are now united in a fresh effort will successfully complete the synthesis of rubber.

The Vulcanization of Rubber

*By E. Kindscher**

Definition of Terms
Old and New Theories of Vulcanization

The term "vulcanization" is ordinarily applied to (1) the treatment of rubber at room temperature *(cold vulcanization)* with dilute solutions of sulfur chloride (usually in carbon disulfide) or with sulfur chloride vapor, or (2) the treatment of rubber with sulfur at higher temperatures *(hot vulcanization)*.[1] After being milled, rubber assumes the plastic state which is necessary for the fabrication of rubber products. The process of vulcanization then transforms the rubber from the plastic state into the elastic condition so essential for practical use. Compared with the unvulcanized product, vulcanized rubber is less sensitive to a wider range of temperature changes, possesses more resistance to tear, and, as far as "soft rubber" is concerned, is more extensible. Its solubility is also greatly affected, for at ordinary temperatures the vulcanized product is no longer soluble in the usual solvents for raw rubber, but is only capable of swelling more or less, depending upon the nature of the solvent and the degree of vulcanization of the rubber. Through vulcanization, rubber obtains most of the properties which make it so unusually valuable as a material for present-day use. Accordingly, almost all rubber goods intended for practical use are vulcanized.[2]

Although vulcanization has long been a process of great importance, only in the last decades, after large quantities of vulcanized goods had been manufactured and used, has the mechanism of the process become the subject for exhaustive scientific research. Charles Goodyear discovered hot vulcanization in 1839, and Alexander Parkes cold vulcanization in 1846. Then for almost fifty years both methods were utilized in the preparation of rubber goods, with little concern about the chemical mechanism of the processes. Although during this period some attempts were made to explain the mechanism of vulcanization, the conclusions which were reached appear very fanciful in the light of present knowledge.

Fawsitt,[3] for example, assumed that cold vulcanization involved the substitution of the hydrogen atoms of the rubber molecule by sulfur, and the simultaneous elimination of hydrochloric acid. Thomson [4] considered chlorine the essentially active constituent of sulfur chloride. Terry [5] denied the importance of sulfur for cold vulcanization, and even attributed the vulcanizing action exclusively to the chlorine of the sulfur chloride.

* Translated by J. E. Whittenberg and F. L. Kilbourne.

[1] For the history of vulcanization *see* p. 4. *Cf.* also p. 334 for the cold vulcanization of rubber with sulfur.

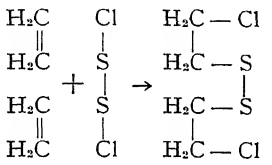
[2] Unvulcanized rubber is largely used in the form of solutions for repairing pneumatic tires, for the cementing of rubberized fabric (manufacture of raincoats, etc.) and for the fabrication of shoes and hat-feathers. Unvulcanized rubber products now on the market usually become vulcanized before they are utilized, although rubber in the unvulcanized state is directly used for shoe soles, in chewing gum, and to an even smaller extent in the manufacture of erasers.

[3] *J. Soc. Chem. Ind.*, **8**, 368 (1889).

[4] *Chem. News*, **62**, 192 (1890).

[5] *J. Soc. Chem. Ind.*, **11**, 970 (1892).

Henriques [6] was the first to establish that sulfur chloride was added as such to the rubber molecule. A year later, this observation was confirmed by C. O. Weber.[7] This addition was supposed to correspond to the reaction which Guthrie [8] had observed in the action of sulfur chloride upon unsaturated compounds such as ethylene and amylene. For example, a compound of the formula $(C_2H_4)_2S_2Cl_2$ was obtained in the case of ethylene. The loosely held chlorine and the firmly bound sulfur of this compound indicated the following explanation of its formation:



Weber deserves the credit of being the first to have investigated thoroughly the chemical nature of vulcanization. In order to determine the composition of the compound which was formed by the action of sulfur chloride upon rubber, he treated at room temperature a filtered solution of 50 grams of purified Para rubber in 1000 cc. of benzene with a solution of 60 grams of sulfur chloride in 200 cc. of benzene (about 120 per cent sulfur chloride on the basis of the rubber.) After some time, this mixture gelatinized. The reaction product was filtered by pressure, using a filter of silk gauze, washed with benzene, extracted in a Soxhlet apparatus with carbon disulfide, and finally treated with boiling alcohol. The resulting product was a yellowish-white powder which was insoluble in the ordinary solvents but soluble in cumene after protracted heating at 140° C. The values obtained by the analysis of the compound agreed very well with the formula $C_{10}H_{16}S_2Cl_2$, for which the theoretical sulfur content is 23.62 per cent. This sulfur content would correspond to the highest possible degree of vulcanization. According to Weber, this compound evolved hydrogen chloride when treated with alcoholic caustic soda solution, and changed quantitatively into a compound of the formula $C_{10}H_{14}S_2$, which has a calculated sulfur content of 32.32 per cent.

However, commercial cold-vulcanized rubber goods never contain as high a sulfur content as is indicated by the formula $C_{10}H_{16}S_2Cl_2$. Henriques stated, for example, that rubber goods containing 5 per cent of sulfur were "over-vulcanized" and those containing 0.5 per cent were "under-vulcanized"; that is, in the first case the highest state of strength and extensibility of the rubber had been exceeded, while in the second case, this point had not yet been reached. Therefore, Weber was not certain whether technical cold-vulcanized products were mixtures of unchanged rubber with the highest sulfur chloride addition product, or whether there existed other definite compounds of rubber with sulfur chloride. To decide this question, he treated a solution of 25.5 grams of rubber in 1000 cc. of benzene with 3 grams of sulfur chloride (11.76 per cent of sulfur chloride on the basis of the rubber). The analysis of the purified reaction product showed it to possess a sulfur content of 5.11 per cent. The compound swelled, but did not dissolve, in benzene.

[6] *Chem.-Ztg.*, **17**, 634 (1893); **18**, 701, 1155 (1894).

[7] *Z. angew. Chem.*, **7**, 112, 142 (1894). Translator's Note. Cf. also *J. Soc. Chem. Ind.*, **13**, 11 (1894).

[8] *Ann.*, **113**, 270 (1860); *cf.* also Ulzer and Horn, *Mitt. tech. Gewerbemus. Wien*, 843 (1890).

Weber concluded that there was present, not a mixture, but a definite compound with a sulfur content of 4.28 per cent and having the empirical formula $C_{100}H_{160}S_2Cl_2$. Upon the basis of the previously mentioned research of Guthrie, this compound should be formulated as $(C_{50}H_{80})_2S_2Cl_2$. Reasoning from the results of these experiments, Weber postulated the compound $C_{10}H_{16}S_2Cl_2$ or $(C_{10}H_{16})_{10}(S_2Cl_2)_{10}$ as the highest attainable vulcanization product, and conjectured that between this compound and the lowest, $(C_{10}H_{16})_{10}S_2Cl_2$, there existed eight other compounds, each of which differed from the next in the series by one molecule of sulfur chloride.

Henriques [9] objected to these broad conclusions soon after their publication. He pointed out that the products analyzed by Weber lacked all the characteristics of definite compounds. "They contain only approximately as much sulfur and chlorine as they should, according to the quantity of sulfur chloride used. There is no proof that when considerably more than 120 per cent of sulfur chloride is used in the vulcanization, the same compound, $C_{10}H_{16}S_2Cl_2$, is formed, and that by the use of less than 9.92 per cent of sulfur chloride a part of the rubber remains unvulcanized, and that therefore no lower stage of vulcanization exists than that corresponding to the formula $C_{100}H_{160}S_2Cl_2$. If these points be confirmed, the proposed formulas will have a somewhat firmer basis." Weber could not ignore these serious objections. After further experiments, he changed his ideas [10] and assigned to the compound corresponding to the lowest degree of vulcanization the formula $(C_{10}H_{16})_{24}S_2Cl_2$ (sulfur content 1.88 per cent) and to the compound representing the highest degree of vulcanization the formula $(C_{10}H_{16})_{24}(S_2Cl_2)_{24}$. Budde,[11] however, stated that he had encountered satisfactorily vulcanized slabs, the vulcanization coefficients [12] of which amounted to 1.03, a value which was considerably lower than that corresponding to the lowest degree of vulcanization as finally accepted by Weber.

Weber's [13] work was not confined to a study of cold vulcanization. He also investigated the process of hot vulcanization. For this purpose he used slabs, 3 mm. in thickness, of a mixture of 100 parts of Para rubber and 10 parts of sulfur, which he vulcanized in strips 30 mm. wide and 60 mm. long, in an autoclave partly filled with water. The vulcanizates, cut into very fine threads, were then extracted with acetone as completely as possible, and the residue was analyzed for combined sulfur by the method of Carius. Weber conducted a series of experiments by this method, using various vulcanization temperatures and times of heating. The results of these tests are shown graphically in Figure 48.

The amount of sulfur combined with the rubber is seen to increase with the time of vulcanization and also with the temperature of vulcanization. The breaks in the curve are due to the formation of definite chemical compounds, according to Weber. These apparent irregularities in the consumption of sulfur later occasioned all sorts of interpretations and hypotheses, until it was finally established that their occurrence could be traced back to a faulty experimental technique.

Since no evolution of hydrogen sulfide was observed during the vulcanization process, there seemed to be no possibility that a substitution reaction was involved. Therefore, an addition of sulfur to the rubber molecule, as in cold

[9] *Chem.-Ztg.*, **18**, 701, 1155 (1894).

[10] C. O. Weber, "The Chemistry of India Rubber," p. 104. Griffin and Company, London, **1902.**

[11] *Gummi-Ztg.*, **21**, 1207 (1907).

[12] By "vulcanization coefficient" is meant the amount of combined sulfur per 100 parts of pure rubber.

[13] C. O. Weber, *Kolloid-Z.*, **1**, 33, 65 (1906).

vulcanization, must have occurred. Further research revealed that with the same vulcanization temperature and the same time of heating, the amount of sulfur combined with the rubber depended upon the amount of sulfur originally present in the mixture. If the vulcanization did consist of the formation of a definite compound of sulfur with rubber, then there should be an upper limit for the amount of sulfur consumed. In order to verify this point, Weber heated a mixture composed of 100 parts of Para rubber and 75 parts of sulfur for eight hours at 140° C. Analysis showed that the product obtained contained 33.11 per cent combined sulfur. When the sulfur content of the mixture was lowered to 50 parts or raised to 100 parts, under the same experimental conditions as before, products were obtained containing 33.08 per cent and 32.64 per cent combined sulfur, respectively. Since a sulfur content of 32.00 per cent corresponds to the formula $C_{10}H_{16}S_2$, which could be formed by the addition of two atoms of sulfur to a rubber molecule ($C_{10}H_{16}$, according to the belief at that time), Weber concluded that this compound was present in his vulcanizates. Although some of his tests showed a slight excess of sulfur, he attributed this to a negligible substitution of the hydrogen atoms of the rubber molecule by sulfur. He also pointed out that apparently the free sulfur contained in the above samples (that is, the sulfur not combined with the rubber) is very difficultly extracted by acetone and even more difficultly with carbon disulfide. It is left open to discussion whether or not the free sulfur may be present in an amorphous form insoluble in carbon disulfide—a form which, under the influence of the warm solvent, is only gradually transformed into the soluble form. He therefore considered it likely that hard rubber represented a concentrated solution of colloidal sulfur in "polyprene sulfide" (the compound $C_{10}H_{16}S_2$).

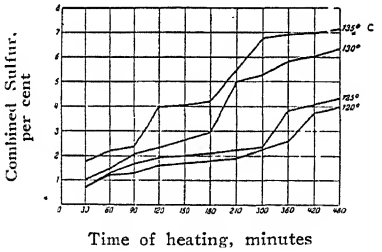


Figure 48—Hot vulcanization (according to Weber).

Misled by the irregular vulcanization curve, Weber further assumed that in hot vulcanization there was involved a continuous series of addition products of sulfur and the rubber hydrocarbon, even as he had assumed in the cold vulcanization of rubber goods. He was not able to identify the lowest member of the series, but concluded that it must be represented by the formula $(C_{10}H_{16})_{10}S$, or $C_{100}H_{160}S$, since according to the knowledge of the process at that time, a combined sulfur content of at least 2 to 2.5 per cent was required for vulcanized rubber, judging from mechanical properties. Physically, this series was characterized by a decrease in extensibility and an increase in strength from the lower to the higher members. Which member of the series occurred in a given vulcanizate depended, in Weber's opinion, upon the temperature and time of heating employed, as well as upon the amount of sulfur present.

Although Weber's ideas were later found to be untenable in many respects, there is no doubt that his work pointed the way for later investigations of both hot and cold vulcanization. Without the information from his experiments, many of the facts observed in the following years would have remained unintelligible. In any case, Weber was the first to learn that in the vulcanization process there took place a purely chemical reaction which was, moreover, an addition reaction.

After Weber's work, there appeared many other investigations of the vulcanization process by the most diverse methods. The hypotheses which were advanced but soon disproved will not be discussed here.[14] Mention may be made of a work by H. Erdmann,[15] which is of interest for later consideration. He assumed that in hot vulcanization an "active thio-ozone" of the formula S_3, present in large amounts in molten sulfur at 160° C., formed an addition product in the same manner as ozone. Vulcanized rubber, according to his idea, is "essentially a semi-solid solution of the polymerized octatomic sulfur, $(S_8)_x$, in the polymerized rubber hydrocarbon and in the thio-ozonide of the latter; hard rubber is a poly-thio-ozonide of rubber."

In contrast to Weber's explanation of the vulcanization reaction from the standpoint of chemical constitution alone, attempts were later made to utilize the principles of physical chemistry, and especially of colloid chemistry, for the solution of this problem. E. Stern [16] was the first to employ quantitative physical measurements in the study of vulcanization. Seeking an unequivocal and easily reproducible method for studying the equilibrium which should exist between the rubber hydrocarbon and sulfur at the temperature of hot vulcanization, he used solutions of sulfur and of rubber. In this way, he could work independently of the transient mechanical and physical properties of the materials used, for these properties might seriously influence direct vulcanization tests. Naphthalene was found to be a suitable solvent for both rubber and sulfur. The first experiments employed the cryoscopic method. No freezing-point lowering of the naphthalene was caused by the colloidal rubber hydrocarbon. Therefore, with a mixture of rubber, sulfur, and naphthalene, the depression of the freezing-point of naphthalene could be influenced only by the concentration of sulfur. The equilibrium, sulfur-naphthalene, had been worked out by Hertz [17] and by van Bijlert.[18] The eutectic point lay at 73.3° C. and at a concentration of sulfur of about 19 to 20 per cent. Assuming that the portion of the sulfur combined with the rubber contributed as little to the lowering of the freezing-point of the naphthalene as did the rubber itself, only the "free" sulfur was considered responsible for the depressions noted. By frequent determinations of the melting-point of solutions of rubber and sulfur in naphthalene at various intervals of time, it should be possible to follow the course of the vulcanization process. The melting-point should rise in proportion to the decrease of free sulfur available, and therefore in proportion to the absorption of the sulfur by the rubber hydrocarbon. The experimental results confirmed these assumptions, although the observed

[14] See R. Ditmar, "Die Analyse des Kautschuks, der Gutta-percha, Balata, und ihrer Zusätze," p. 62, A. Hartleben's Verlag, Vienna and Leipzig, **1909**; Axelrod, *Gummi-Ztg.*, **24**, 352 (1909); Hübener, *Chem.-Ztg.*, **35**, 494 (1911).

[15] *Ann.*, **362**, 133 (1908).

[16] *Chem.-Ztg.*, **33**, 756 (1909); *Z. Elektrochem.*, **15**, 660 (1909).

[17] *Z. phys. Chem.*, **6**, 358 (1890).

[18] *Z. phys. Chem.*, **8**, 343 (1891).

changes in melting-point of the naphthalene were too small to permit definite conclusions.[19]

Stern then tried to obtain more information about the course of the vulcanization process by direct analysis of samples taken at definite intervals of time. The reaction mass was poured into acetone, the precipitated rubber was exhaustively extracted with acetone in a Soxhlet apparatus, and a determination was made of the combined sulfur in the extracted residue. In the preliminary experiments, the temperature and time of vulcanization were held constant. The results seemed to substantiate the relation stated by Hübener,[20] who found, by direct vulcanization experiments, that the amount of sulfur absorbed by the rubber was approximately proportional to the original amount of sulfur added. In Stern's later experiments, the composition of the reaction mixture and the temperature of vulcanization were kept constant. Under these conditions it was shown that the amount of combined sulfur increased almost in proportion to the time of heating.

The work published up to this time concerning hot vulcanization was summarized by W. Ostwald,[21] and was examined by him from an entirely new point of view—that of the adsorption theory. Ignoring the possibility of the formation of a definite chemical compound between rubber and sulfur, he concluded that the previously reported results of qualitative and quantitative tests concerning the action of sulfur on rubber could be explained by the assumption of adsorption alone. Among the points of support which he listed for his views were the following:

1. As J. B. Höhn [22] had established, there always exists in a vulcanizate a portion of the sulfur in the "free," acetone-soluble form, whether a large or a small amount of sulfur is added originally. A theory of purely chemical addition should require that a very small amount of sulfur be entirely consumed in a short time.

2. According to Weber, the evolution of small amounts of hydrogen sulfide during vulcanization is traced back to the presence of impurities in the rubber, and the combination of sulfur with rubber is a purely additive process. This fact Ostwald also considered to be in accord with the adsorption theory.

3. Weber's conception that rubber forms with sulfur a continuous series of addition products would first have to be demonstrated by the actual discovery of some definite compounds. However, Weber could prove the existence of only a single compound of this sort, and at the time there existed no possibility of separating and distinguishing the different products corresponding to the degrees of vulcanization which he formulated. In fact, according to Ostwald, the continuity of change of composition directly indicated an adsorption process.

4. The composition of the lowest and the highest members of the series of vulcanization compounds postulated by Weber is indefinite and is not sufficiently proved.

[19] It should be mentioned that E. Stern was the first to accomplish the hot vulcanization of rubber in solution.

[20] *Gummi-Ztg.*, **24**, 214 (1909).

[21] *Kolloid-Z.*, **6**, 136 (1910).

[22] *Gummi-Ztg.*, **14**, 17, 33 (1899). On account of the lack of a mathematical relationship between the amount of unextractable sulfur and the physical properties of the vulcanizate, Höhn was led to infer that "vulcanization is not a chemical reaction, but the melted sulfur becomes absorbed in the cells of the rubber, forming a solution the physical properties of which are different from those of the original material."

5. Axelrod[23] was able to establish quantitatively that the amount of sulfur combined during vulcanization depends to a great extent upon the previous mechanical treatment of the rubber. From the standpoint of the adsorption theory, this fact may be explained by saying that rubber, as a colloid, has a polyphase structure, by the mechanical working of which is produced an intimate mixing of the various phases and an additional surface suitable for adsorption.

6. From calculations based upon Weber's data concerning the amount of sulfur absorbed for equal times but at different temperatures, temperature coefficients are obtained which correspond more nearly with those of adsorptions than those of typical chemical reactions. In the case of chemical reactions, the reaction velocity increases from 2 to 3.5 times for a temperature rise of 10° C., according to van't Hoff, while in adsorption there is an increase of less than 1.5 times.

7. To explain the breaks in Weber's vulcanization curves for various temperatures, Ostwald called attention to the fact that phenomena of this kind had been frequently observed with adsorption curves, and had been interpreted as being caused by capillary-chemical influences.

8. When it was assumed that a proportionality prevailed between the amount of sulfur added to the mixture and that taken up by the rubber, the calculation of Stern's data showed an error of 11.6 per cent as the largest deviation. When the adsorption equation (*see* p. 278), $\frac{x}{a} = k \cdot c^{\frac{1}{n}}$, was used for the calculation, this error was found to be only 0.79 per cent. Similar values were obtained from the vulcanization experiments of Hübener.[24] Such results are more in harmony with the adsorption theory than with a theory based upon chemical reaction. It seemed strange that the curves which show the dependence of the amount of combined sulfur on the amount of sulfur added, show opposite curvature in the experiments of Stern and Hübener. Ostwald explained this by saying that when sulfur was taken up by rubber, there was involved a mutual adsorption of two disperse phases—namely, the emulsoid rubber, and the rubber distributed in this disperse phase. At definite quantity-ratios of the two disperse, mutually adsorbed phases, these must interchange their roles, so that the adsorbent becomes converted to the adsorbed substance.

Ostwald's adsorption theory was at first generally accepted, since it seemed very plausible, assuming the correctness of the experimental foundation. However, various objections were soon raised which could not be ignored. Nevertheless, it is to Ostwald's credit that he brought the problem of vulcanization again into the focus of interest and called the attention of investigators to points which urgently needed proof.

P. Alexander,[25] from his knowledge of the reclaiming of rubber, stated that there was no possibility of again removing the sulfur of vulcanization from a vulcanizate. He also pointed out that in the formation of the bromide and the nitrosite of rubber, the sulfur passes into the derivative. F. W. Hinrichsen[26] then advanced a series of important arguments against Ostwald's views, and suggested that not only adsorp-

[23] *Gummi-Ztg.*, **24**, 352 (1909).
[24] *Gummi-Ztg.*, **24**, 214 (1909).
[25] *Chem.-Ztg.*, **34**, 789 (1910).
[26] *Kunststoffe*, **1**, 41 (1911).

tion phenomena but also purely chemical reactions occurred during the course of vulcanization. His contentions were as follows:

1. It appears, especially from the work of Freundlich,[27] that in adsorption there is always concerned an equilibrium which can be approached from both sides. Therefore, if only adsorption plays a part in the taking up of sulfur by rubber, the process should be reversible. It is generally known that this can be realized only with the greatest difficulty, if at all; in fact, most practical chemists regard the complete desulfurization of vulcanized rubber as a problem which cannot be solved. While the latter idea may not be entirely correct, the desulfurization of vulcanized rubber is so difficult that the assumption of an adsorption equilibrium for the explanation of vulcanization seems unsafe, to say the least. Such equilibria are characterized by the rapidity with which they are established.

2. When an adsorption equilibrium is attained, the chemical and physical properties of the adsorbed and the adsorbing substances usually remain unaltered. However, rubber undergoes during vulcanization a transformation as complete as that usually encountered only with chemical change. This is true also of the sulfur consumed in hot vulcanization. The sulfur becomes partly insoluble in the usual solvents, such as acetone, so that in the analysis of rubber goods a distinction is made between the acetone-soluble "free" sulfur and the acetone-insoluble "combined" sulfur.

It is possible to cite cases where a complete change in behavior of a substance is observed when it becomes adsorbed. In the work of Freundlich and Losev[28] on the adsorption of basic dyestuffs (such as crystal violet) upon carbon, it was shown that after the establishment of equilibrium, no more of the dyestuff could be washed out with pure water. However, in this case, as Freundlich and Losev were able to show, chemical change occurred as well as adsorption. The crystal violet in the form of the hydrochloride had quantitatively yielded to the aqueous solution the hydrochloric acid contained in it, and only the dye-base was adsorbed by the carbon. Since the base itself is not soluble in pure water, it could not be removed by the aqueous solution. If water is replaced by a suitable solvent or an acid, a portion of the dye-base redissolves at once.

3. The formation of a chemical compound during vulcanization is strongly indicated by the fact that all of the sulfur of vulcanization is found in derivatives such as the tetrabromide and the nitrosite. This behavior was observed by Alexander.[29] Since the derivatives are partly precipitated from solutions of vulcanized rubber (for example, in the determination of rubber according to Axelrod),[30] it must be supposed that the original adsorption equilibrium between solid rubber and sulfur was disturbed by the solution process.

4. The assumption of the existence of a definite chemical compound of rubber and sulfur seems reasonable, since other well-defined compounds of rubber, such as the tetrabromide, are definitely known.

These discussions served to expound the conflicting views to some extent, and experimental work was then continued along both the physical

[27] *Z. phys. Chem.*, **57**, 385 (1906).
[28] *Z. phys. Chem.*, **59**, 284 (1907).
[29] *Chem.-Ztg.*, **34**, 789 (1910).
[30] *Gummi-Ztg.*, **21**, 1229 (1907).

and chemical lines of investigation. The intensive research of the following years resulted in an abundance of publications concerning the problem of vulcanization. Only the most important of these can be treated in detail.

Hinrichsen and Meisenburg [31] repeated the experiments of Weber concerning cold vulcanization, in order to establish whether a definite compound could be obtained by the method Weber employed. They treated solutions of Para rubber in benzene with a larger amount of sulfur chloride than corresponded to the highest vulcanization stage assumed by Weber. Eight different reaction products, purified according to Weber's method, were found to have a sulfur content of from 15.58 to 28.37 per cent. These workers could not obtain values which agreed with each other even approximately. It is to be noted that some sulfur values were obtained which were below that corresponding to the formula $C_{10}H_{16}S_2Cl_2$ (23.62 per cent sulfur) proposed by Weber. Since the isolated compound was extracted only with carbon disulfide for the removal of excess sulfur, it seems unlikely that any of the combined sulfur could have been removed from the compound in this manner. Therefore, if a substance of definite composition was really present, the lowest of the sulfur values found must be assumed to be the most nearly correct. The higher values may be explained by the impossibility of removing the sulfur chloride still adhering by adsorption to the addition product, or, more probably, by the impossibility of removing completely from the addition product the sulfur separated by atmospheric moisture or by treatment with alcohol. The latter explanation is the more plausible, because the free sulfur settled out of sulfur chloride is partly insoluble in carbon disulfide. However, it is one of the most characteristic properties of colloids that they can build adsorption compounds.

Since the use of direct analysis failed to settle the question, Hinrichsen and Kindscher [32] tried an indirect method. Exact amounts of solutions of rubber and of sulfur chloride in benzene were mixed together. After standing for many weeks, the mixed solution contained a precipitate, and a portion of the supernatant liquid was analyzed. The consumption of sulfur chloride could be determined from the chlorine content of this liquid, and thus it could be decided whether there had been formed a chemical compound of definite composition or an adsorption compound. In an adsorption, the equation $\frac{x}{a} = k \cdot c^m$ would show the dependence of the consumption of sulfur chloride (x) upon the initial concentration of sulfur chloride (c). In this equation (a) represents the concentration of rubber, while (k) and (m) are constants. If a chemical compound is formed, the consumption of sulfur chloride must be constant. It was found by these experiments that the consumption of sulfur chloride by equal amounts of rubber was approximately constant. Small deviations may be explained by slight losses due to the volatilization of the sulfur chloride, which could not be entirely avoided. Such losses would cause too low a chlorine content of the solution to be found by the indirect analysis, and therefore somewhat high values would be assumed for the consumption of sulfur chloride. The data showed that rubber absorbs one-half of its weight of sulfur chloride. Since the formula of rubber was at that time considered to be $(C_{10}H_{16})_x$, Hinrichsen and Kindscher

[31] *Chem.-Ztg.*, **33**, 756 (1909). [32] *Kolloid-Z.*, **6**, 202 (1910).

assigned to the compound formed the formula $(C_{10}H_{16})_2S_2Cl_2$, which would mean that the reaction was parallel to that found by Guthrie with ethylene and amylene (*see* p. 271). These results directly contradicted those obtained by Weber, but agreed with those of Hinrichsen and Meisenburg in that the lowest sulfur value obtained by the latter workers corresponded exactly to the formula $(C_{10}H_{16})_2S_2Cl_2$.

Further support for this formula was seen by Hinrichsen and Kindscher in the behavior of the sulfur chloride addition product when treated with an alcoholic solution of sodium hydroxide. After protracted heating with this caustic solution, there was formed a dark brown, hard substance, which contained no chlorine and which contained 20.7 per cent of sulfur. Assuming that a compound $(C_{10}H_{16})_2S_2Cl_2$ could evolve two molecules of hydrogen chloride under these conditions, a compound $C_{20}H_{30}S_2$ would be obtained, with a sulfur content of 19.2 per cent. On the contrary, Weber had obtained under the same experimental conditions a compound, the sulfur content of which, 32.3 per cent, indicated a composition corresponding to $C_{10}H_{14}S_2$. The disagreement of the results of Hinrichsen and Kindscher with those of Weber was explained by G. Bernstein, as will be later discussed.

No definite conclusion was reached from the work of Hinrichsen, Kindscher, and Meisenburg as to whether in technical cold vulcanized rubber goods there existed definite chemical compounds. However, no evidence was revealed for the existence of other than the highest vulcanization product. Therefore it was concluded that in products which contained less sulfur chloride than corresponded to the highest vulcanization stage, there occurred a sort of solid solution of the addition compound in excess rubber. It was held probable that adsorption processes played some part in the cold vulcanization of rubber goods because of the colloidal nature of rubber and because of the method of preparation of commercial vulcanizates. In the industrial process, the moisture of the air causes some sulfur to separate from the sulfur chloride, but this is not a factor in scientific work. Hinrichsen believed that cold-vulcanized rubber goods represented adsorptions of sulfur in "solid" or "semi-solid" solutions of the sulfur chloride addition product in excess rubber. In this connection, it should be mentioned that it was Höhn [33] who first made the observation that better results were obtained in vulcanization by the use of sulfur chloride solutions which contained excess dissolved sulfur than by the use of those containing no excess sulfur.

Further work on the explanation of the chemical mechanism of cold vulcanization was reported by B. Bysow.[34] Solutions of rubber were not used in this work. Instead, the technical execution of cold vulcanization was simulated by dipping slabs of Para rubber of 0.5 gram weight, 0.5 mm. thickness, and of as nearly equal surface areas as possible, in very dilute solutions of sulfur chloride in benzene. At regular intervals of time, determinations of the sulfur content of the vulcanizate were made, after removing the excess sulfur chloride. Bysow found that these values increased rapidly at first, then more slowly, and finally remained almost constant. Similar results were obtained when the Para slabs were allowed to remain for equal lengths of time in benzene solutions

[33] *Gummi-Ztg.*, **14**, 17, 33 (1899); cf. also G. Bruni and M. Amadori, *India Rubber J.*, **58**, 129 (1919).

[34] *Kolloid-Z.*, **6**, 281 (1910); *J. Russ. Phys. Chem. Soc.*, **53**, 20 (1921).

of sulfur chloride of various concentrations (from 0.0125 to 0.1 gram in 100 cc.). Therefore, it appeared that the sulfur chloride was taken up strictly according to the equation $\frac{x}{a} = k \cdot c^m$, according to the adsorption law.

The very contradictory conclusions drawn by Hinrichsen and Kindscher and by Bysow were interpreted by Wo. Ostwald [35] from a single point of view in a very clever manner. Bysow had used very dilute solutions, while Hinrichsen and Kindscher had worked with much higher concentrations. Ostwald stated that the differing experimental results could be reconciled to the adsorption theory if the concentrations of sulfur chloride were plotted against the amounts of sulfur chloride consumed by the rubber. When this is done, it is seen that the results of Bysow lie in the rising portion of the curve (concentrations from 0.0125 to 0.1 per cent sulfur chloride), while the results of Hinrichsen and Kindscher, who worked with concentrations of sulfur chloride varying from 1.237 to 2.362 per cent, lie in the part of the curve which proceeds parallel to the abscissa.

These investigations did not aid materially in reaching a definite decision in favor of either the adsorption theory or the chemical theory. G. Bernstein [36] then undertook further experiments, and succeeded in demonstrating the cause of the disagreement in the results of Weber and of Hinrichsen and Kindscher. He showed that when the reaction product of rubber with sulfur chloride was treated with alcohol, as Weber had done to purify his products, hydrogen chloride was evolved. The values obtained by Weber must have been accidental, since the analyzed products were mixtures of sulfur chloride addition products with their decomposition products. Bernstein proceeded to eliminate these sources of error, and obtained, by the analysis of the reaction products, values which agreed very well with the formula $(C_{10}H_{16})_2S_2Cl_2$. The results of Hinrichsen and Kindscher were thus confirmed. Bysow's results, which had been used by Ostwald to support his contention that the absorption of sulfur chloride by rubber was an adsorption phenomenon, were also readily interpreted by Bernstein from a purely chemical standpoint. The rubber slabs which were dipped into sulfur chloride solutions became quickly coated with a layer of the reaction products, which retarded the penetration of sulfur chloride into the interior of the strip, and finally brought the process to a standstill. In order to demonstrate this point, Bernstein measured the viscosities of mixtures of rubber and sulfur chloride using xylene as a mutual solvent. Mixtures of varying concentrations were tested. The viscosity of xylene itself is not influenced by the addition of sulfur chloride. If only an adsorption of sulfur chloride on the rubber occurred, Bernstein reasoned that the viscosity of the rubber solution should increase upon the addition of sulfur chloride, since a constantly increasing volume of the colloid particles, with an accompanying increase of the specific surface of the phases, should result in greater surface friction of the phases. However, the addition of sulfur chloride was found to reduce the viscosity of the rubber solutions. Therefore, an adsorption phenomenon was not indicated by these results.

[35] Z. Chem. Ind. Kolloide, 7, 45 (1910).
[36] Dissertation, June 13, 1912, Clermond-Ferrand, "Contribution à l'étude de la vulcanization à froid du caoutchouc."

M. Le Blanc and M. Kröger [37] later called attention to the fact that all vulcanizations in solution, from a purely objective viewpoint, consisted of the solution becoming less viscous, followed by gel formation in the case of high rubber concentrations and by a flocculation with low rubber concentrations. Between these extremes, intermediate phenomena are observed. Gel formation is followed by the expressing of serum at sufficient concentrations of sulfur chloride (syneresis). These authors observed experimentally that syneresis was perceptible after some days if the amount of sulfur chloride used was somewhat in excess of that necessary for the formation of the compound described by Hinrichsen and Kindscher. A gel containing only 20 per cent of sulfur chloride upon the basis of the rubber expressed no serum within a time of six months. From these observations, it was thought that the syneresis was dependent upon the complete consumption of the rubber. This conclusion was supported by the fact that in a gel which normally did not show syneresis, the latter phenomenon occurred upon the addition of bromine, in proportion to the extent that the bromine diffused into the gel. The unconsumed rubber was converted by the bromine into the tetrabromide. In dilute solutions of rubber, the "flocking" corresponds to syneresis. The flocculation first occurs when the composition of the compound of Hinrichsen and Kindscher is reached. If the amount of sulfur chloride is kept too small, separation in flocks can be effected by the addition of sufficient bromine, as in the case of syneresis. Addition of materials which do not form derivatives of rubber has no effect. An exception to this statement was found in the case of vulcanization accelerators, which probably form no rubber derivatives, but allow the earlier occurrence of exudation when otherwise insufficient amounts of sulfur chloride are present. (*See* p. 316.)

The work of Bernstein and of Le Blanc and Kröger therefore fully confirms the results found by Hinrichsen and Kindscher, so that it may now be taken as certain that the action of sulfur chloride upon rubber is a chemical one, and that rubber can combine with half its weight of sulfur chloride. What proportion applies in technical cold-vulcanized rubber goods, which contain much less sulfur chloride than corresponds to the highest vulcanization stage, still remains unknown.

It may be mentioned here that in the scientific investigations there was usually employed a sulfur chloride (which was obtained by the purification of the technical product), the composition of which corresponded to the formula S_2Cl_2. Doubtless this accounts for the difference between the laboratory and factory vulcanization processes, which difference is shown by the fact that technical products frequently contain more sulfur than corresponds to the ratio (Cl:S). G. Bruni and M. Amadori,[38] who have studied this question thoroughly, believe that this can be explained by the formation of polythiochlorides. They proved that a solution of pure sulfur chloride in bromoform showed a freezing-point lowering which corresponded to the formula S_2Cl_2. However, mixtures of sulfur chloride and sulfur in the same solvent gave a somewhat smaller freezing-point lowering than corresponded to the sum for the individual substances. It therefore seemed that polythiochlorides were present in such solutions. If the values found and calculated are compared with each other, and if the approximate formula of the complex is ascertained

[37] *Z. Elektrochem.*, **27**, 335 (1921). [38] *India Rubber J.*, **58**, 129, 171 (1919).

mathematically, it is found that in bromoform solution, the highest of these complexes conforms to the formula S_4Cl_2. It is probable that there are present chlorides with even higher sulfur contents (ClS_nCl). Because of the presence of these polythiochlorides, poly-thio derivatives are formed by the treatment of organic compounds with technical sulfur chloride, and so there are formed in the cold vulcanization of rubber, products which contain sulfur in higher ratios than S:Cl. The polysulfide sulfur from such poly-thio derivatives is probably split off, and in the nascent state is able to add to the double bonds of the rubber hydrocarbon (*see* p. 321).

These studies of cold vulcanization followed many investigations of the chemical mechanism of hot vulcanization. Hinrichsen [39] again took issue with Wo. Ostwald, and pointed out that adsorption equilibria were usually attained more rapidly than was the case in the chemical reactions of undissociated organic compounds. According to Hinrichsen, although the typical colloid nature of rubber pointed directly to the assumption that in vulcanization pure surface adsorption of the vulcanizing agent took place primarily, many authorities on rubber cite phenomena which show that after the adsorption, chemical union of the adsorbed material occurs. If this is true, then the second part of the process, the chemical union, occurs not only at temperatures which are ordinarily used for hot vulcanization (above the melting point of sulfur), but also at any temperature whatever. Naturally, however, the velocity of the reaction will be less if the existing temperature is lower. The phenomenon of "after-vulcanization" agrees with these theoretical considerations. If hot-vulcanized rubber goods which contain "free" sulfur are stored for a long time, the amount of sulfur combined with the rubber increases more or less rapidly, depending upon the kind of storage and the type of rubber mixture. These processes have been studied more in detail in the Materialprüfungsamt at Berlin-Dahlem, with a vulcanizate of Para rubber and sulfur. The results of these experiments are evident from Table 1.

TABLE 1.—*Sulfur Determinations in "After-Vulcanized" Samples.*

Kind of Storage	Total sulfur per cent	Free sulfur per cent	Combined sulfur per cent
Original sample	9.0	4.5	4.5
6 months, room temperature, dark, moist	8.9	4.3	4.6
6 months, room temperature, dark, dry	9.0	4.1	4.9
6 months, on roof	8.4	2.3	6.1
6 months, at about 70° C., dark, moist	8.5	2.0	6.5
6 months, at about 70° C., dark, dry	8.6	1.1	7.5

Therefore, it is seen that the vulcanization process, when once induced, proceeds slowly at room temperature. These results raise the question as to whether a gradual union of sulfur with rubber in unvulcanized mixtures also takes place at ordinary temperatures. Hinrichsen and Kindscher [40] sought to answer this question by the study of two mixtures, one containing only rubber and sulfur, and the other containing rubber, sulfur, and litharge, which is known to increase the rate of vulcanization. Samples were cut from slabs of 1 mm. thickness, and were kept

[39] *Kol.-Z.*, **8**, 245 (1911). *Cf.* also J. Minder, *Gummi-Ztg.*, **14**, 248 (1900).

[40] *Z. Elektrochem.*, **18**, 531 (1912).

for 18 months, with exclusion of air, some in the dark and some in the daylight, and were then analyzed. It was found that a distinct, although slight, combination of the sulfur had begun, especially in those samples which had been exposed to the action of daylight.

D. Spence[41] thoroughly studied the influence of low temperatures on the rate of hot vulcanization and "after-vulcanization." Both vulcanized and unvulcanized samples were exposed for several months to various atmospheric conditions and temperatures, and the changes taking place were ascertained by complete analysis. For these tests, Spence selected two mixtures of well-purified rubber with about 9 per cent sulfur. The one of them which was "slow-vulcanizing" inclined to quicker decomposition than the one which was "quick-vulcanizing,"[42] the latter showing less decomposition phenomena after a long time. The unusually interesting results are reproduced in Tables 2 and 3.

TABLE 2.—*Slow-Curing Mixture.*

	Unvulcanized		Under-Vulcanized		Normal Vulcanized		Over-Vulcanized	
Experimental Conditions	Resin content per cent	Combined S per cent	Resin content per cent	Combined S per cent	Resin content per cent	Combined S per cent	Resin content per cent	Combined S per cent
Initial value	1.06	.....	1.31	3.05	1.82	4.32	2.18	5.91
Sample in dark room (3 months)	1.37	0.05	4.55	3.71	4.54	5.01	3.66	6.56
Sample in sunlight (3 months)	1.46	0.07	4.54	3.64	4.74	4.94	3.78	6.50
Sample in thermostat (3 months at 40° C.)	1.48	0.11	4.87	4.14	4.78	5.46	3.97	7.02

TABLE 3.—*Quick-Curing Mixture.*

	Unvulcanized		Under-Vulcanized		Normal Vulcanized		Over-Vulcanized	
Experimental Conditions	Resin content per cent	Combined S per cent	Resin content per cent	Combined S per cent	Resin content per cent	Combined S per cent	Resin content per cent	Combined S per cent
Initial value	2.53	0.193	2.78	0.876	2.85	2.502	.....	3.353
Samples in dark room (3 months)	2.36	0.205	2.24	0.969	2.30	2.615	2.34	3.741
Samples in sunlight (3 months)	3.85	0.244	3.58	0.901	3.50	2.539	3.59	3.620
Samples in thermostat (3 months at 40° C.)	2.29	0.350	2.36	1.086	2.26	2.801	2.35	3.888

It may be seen that in rubber mixtures which do not tend to deteriorate during a storage of three months under ordinary atmospheric conditions, as well as at 40° C., little if any vulcanization occurs. Whether the samples be kept in daylight or dark is immaterial. However, mixtures in which decomposition phenomena appear show under the same conditions an appreciable, and in some cases a considerable, increase in the amount of combined sulfur. Spence also sought to determine the temperature at which appreciable vulcanization became evident. He used two "quick-vulcanizing" mixtures, pigment-free and not inclined to decom-

[41] *Kolloid-Z.*, **10**, 299 (1912).

[42] Upon what the property of "quick vulcanization" of the mixture depended is not indicated in the work.

Translator's Note. According to Spence, the "quick-curing" mixture contained piperidine as an accelerator. *See* p. 19, and *J. Soc. Chem. Ind.*, **36**, 118 (1917).

position, with about 9 per cent of sulfur, and heated samples of these in sealed glass tubes in a thermostat at 50°, 65°, 80°, 95°, and 110° C. The combined sulfur content of these samples was determined after 1, 3, 6, and 9 days. The results showed that vulcanization in the mixtures not inclined to decomposition was very slight after 9 days at temperatures up to about 60° C., but was quite appreciable at 80° C. These findings created the impression that somewhere in the neighborhood of 60° C. there lay a "reaction temperature," at which the vulcanization proceeded very quickly, but below which practically no combination of sulfur took place. The most important thing which these tests showed, however, was that the view widely quoted in the literature since Höhn and Minder—that rubber cannot be so vulcanized that all the free sulfur disappears—was erroneous. Spence, in fact, was able to show that a complete consumption of free sulfur can be attained at temperatures below those employed in technical vulcanization. In this manner was refuted one of the strongest arguments in favor of the physical-chemical adsorption of combined sulfur.

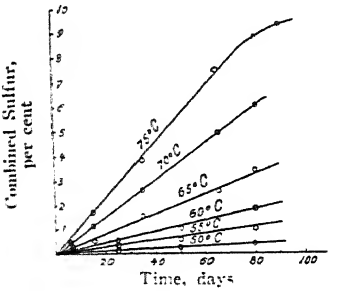


Figure 49—Hot vulcanization at 50° to 75° C.

In a later publication, Spence and Young [43] settled the question of whether there actually existed a "reaction temperature" or "critical temperature" at which the rate of vulcanization suddenly changed, and above which vulcanization progressed regularly with increasing temperature. They studied the rate of vulcanization of two mixtures consisting of rubber and 10 per cent of sulfur in the temperature range of 50° to 75° C., at temperature intervals of 5° C. The first mixture, which contained the purest acetone-extracted and therefore resin-free rubber, vulcanized so slowly that after 90 days at 75° C., the amount of sulfur taken up by the rubber was extremely slight (0.32 per cent). The gradually increasing amount of unextractable sulfur with increasing time signified, however, that a slow vulcanization was taking place in this case. In the second mixture, which contained 1 per cent of acetone-soluble constituents, a vulcanization occurred at 50° C. As can be seen from Figure 49, a fully proportional and definite increase of the vulcanization rate occurs with increasing temperature, and by calculation of the temperature coefficient, or the increase of reaction velocity for each 10 degrees rise of temperature, it is found that the value obtained lies well within the limits for chemical reactions, according to van't Hoff. The average temperature coefficient is 2.84. It was proved that a "critical temperature" does not exist, but that the vulcanization of rubber takes place at all temperatures.

[43] *Kolloid-Z.*, **13**, 265 (1913).

In a series of later, more important publications, D. Spence stated his position in regard to several points which, according to Wo. Ostwald (*see* p. 275), should support the physical-chemical conception of the vulcanization process.

Spence and Scott [44] first established that the severest treatment of vulcanized rubber with boiling alkalies is not able to extract more than a small part of the so-called "combined" sulfur. A further objection to the adsorption theory was seen in the fact that reclaimed rubber (in which the rubber is not devulcanized) (*see* p. 342) consumed during vulcanization the same amount of sulfur, and combined with the same amount, as it required originally. Even if it is assumed that by the reclaiming process, the degree of distribution of the dispersed phase has increased, it still seems unlikely that by increasing the absolute surface of the adsorbing substance the adsorbing power has more than doubled, and that this adsorption capacity can continue to increase until finally the original rubber has adsorbed more than one-fifth of its weight of sulfur.

A third and even more important objection to the physical-chemical theory is seen in the behavior of vulcanized rubber upon bromination, as P. Alexander [45] had pointed out previously. It appeared that the sulfur of vulcanization entered quantitatively into the bromination product, and by careful bromination, a stoichiometrical relation undoubtedly existed between combined sulfur and bromine, whereby $S = Br_2$. The capacity of vulcanized rubber to be brominated is dependent upon its equivalent content of sulfur of vulcanization. Since the change which takes place upon the bromination of the unsaturated rubber hydrocarbon undoubtedly consists of the addition of bromine to the unsaturated bonds of the hydrocarbon, then it follows directly that vulcanization probably depends upon the saturation of the double bonds of rubber by sulfur, which process is assumed to be incomplete in the case of soft rubber. It is likely to be difficult to use the physico-chemical adsorption theory as a basis for the explanation of the stoichiometrical relationship between sulfur and bromine in the bromine derivative of vulcanized rubber.

Spence and Scott further observed that the free sulfur could not be quantitatively removed by a day-long extraction of vulcanized rubber with acetone, and that the course of the extraction is similar to that of the extraction of electrolytes from gelatin with water. As long as large amounts of free sulfur are contained in the vulcanizate, free sulfur is extracted at the same rate. When only small amounts are present, however, the amount of sulfur removed in equal intervals of time is not the same, and the average curve of the extraction assumes the form of an adsorption isotherm. Spence and Scott concluded that the so-called "combined" sulfur is chemically bound to the rubber, but that an adsorption of sulfur also occurs during the vulcanization, and that this adsorption is limited to the "free" sulfur (*see* p. 289). The so-called "free" sulfur therefore is made up of adsorbed sulfur and a greater or less amount of actually "free" sulfur, the amount of which depends upon the state of vulcanization. These authors also assume, as did Hinrichsen,

[44] *Kolloid-Z.*, **8**, 304 (1911); *cf.* also B. W. Bysow and M. K. Popowa, *J. Russ. Phys. Chem. Soc.*, **53**, 65 (1921).

[45] *Chem.-Ztg.*, **34**, 789 (1910).

that the adsorption is an essential step which precedes chemical union in the vulcanization process.

Spence and Young[46] thoroughly investigated the course of vulcanization. The purest Ceylon Para rubber, which had been extracted with acetone and was therefore free from resins, was vulcanized with 10 per cent of sulfur at temperatures of 135° C. and 155° C., in an apparatus which could be maintained at constant temperature. The vulcanized samples were then thoroughly extracted with acetone, and the combined sulfur was determined in the extracted samples. The experimental data are plotted in the two curves of Figure 50, which show that vulcanization proceeds continuously since no breaks are observed in the curves. The widely discussed breaks of Weber's curves (*see* p. 273) are probably due to experimental error. Furthermore, Spence's earlier experimental results could be confirmed, as the total available free sulfur was consumed after vulcanization had been continued 20 hours at 135° C. From the results obtained at 155° C., the temperature coefficient of the reaction was calculated. This coefficient was used as an argument against the adsorption theory, as the value was found to be 2.65, a figure well within the limits assumed for chemical reactions. It was, therefore, fully in accord with a chemical conception of the vulcanization process.

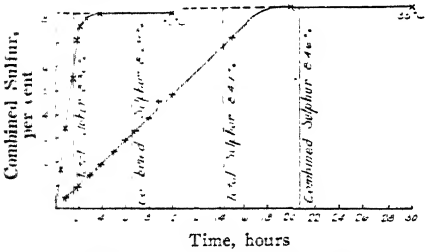


Figure 50—Hot vulcanization at 135° and 155° C.

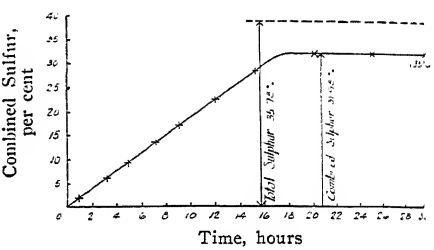


Figure 51—Hot vulcanization (according to Spence).

Spence and Young also prepared a mixture of resin-free rubber with 37 per cent sulfur. This mixture, which contained 5 per cent more sulfur than would correspond to the highest stage of vulcanization ($C_{10}H_{16}S_2$) as described by Weber, was vulcanized at 135° C. in the apparatus previously mentioned. The experimental data are plotted in Figure 51. Here also a non-hyperbolic curve free from breaks was obtained. The highest value for combined sulfur content, 31.97 per cent, was reached after vulcanization for 20 hours. No more sulfur combined with the rubber after longer heating. The maximum figure obtained for combined sulfur agreed very well with the empirical formula $C_{10}H_{16}S_2$. The difference between these results and those obtained by earlier investigators (C. O. Weber, for example) can only be ascribed to the inadequacy of experimental apparatus and to the impurities in the materials used in the earlier work.

The observation of Spence and Young[47] that resin-free gutta-percha and balata react with sulfur in a manner similar to rubber is also of interest.

[46] *Kolloid-Z.*, **11**, 28 (1912).
[47] *Kolloid-Z.*, **11**, 33 (1912); **13**, 269 (1913). Wo. Ostwald [*Kolloid-Z.*, **11**, 34 (1912)] contradicts the views of Spence and Young, without introducing any experimental evidence or any new theoretical viewpoint.

As evidence for his adsorption theory, Wo. Ostwald has cited an investigation of Axelrod,[48] according to which the amount of sulfur taken up during vulcanization should depend to a considerable extent upon the previous mechanical treatment of the rubber. Later work by Spence and Ward,[49] however, by no means confirmed the results of Axelrod. It was shown that, by lengthy mastication of the rubber-sulfur mixture on hot rolls, the mechanical properties of the vulcanizate were unfavorably influenced, but that the affinity of the rubber for sulfur was not changed. Two 100-part samples of the same Para rubber were masticated on hot rolls, one for 30 minutes, the other for 1½ hours, and within ten more minutes each was mixed with 10 parts of sulfur. Examination of the samples after vulcanization showed that, under the same experimental conditions, the sample which had been masticated for a longer time did not combine with sulfur more rapidly than the one which had been masticated for a shorter time.

The investigations of Spence and his co-workers satisfactorily demonstrated the unreliability of the experimental data cited by Wo. Ostwald when he advanced the adsorption theory. Spence summarized the experimental results obtained as follows:

1. Vulcanization is a chemical reaction, and obeys the laws which are valid for chemical reactions.

2. Vulcanization may take place at all temperatures, and progresses slowly or rapidly, according to the conditions under which it occurs. The temperature coefficient of vulcanization lies within the limits assumed for chemical reactions.

3. The reaction progresses quite regularly, and reaches its end-point when a compound containing 32 per cent of sulfur has been formed. If the formula of rubber is assumed to be $(C_{10}H_{16})_n$, in every case the final product of vulcanization is a compound of the formula $(C_{10}H_{16}S_2)_n$.

Hinrichsen and Kindscher[50] also investigated the reactions which occur during hot vulcanization. They were able to verify the essential parts of the experimental results of Spence. In order to obtain clear and easily reproducible results, the vulcanization was performed in solution. A constant volume of a 2 per cent solution of Hevea plantation rubber in pseudo-cumene was heated with increasing amounts of sulfur for periods of 4 and 8 hours. The reaction mixture was then allowed to stand until the excess sulfur had separated. After filtration, the solution was added dropwise, with thorough stirring, to three or four times its volume of acetone, and was allowed to stand overnight. During this time the precipitate which had formed, settled. The precipitate was thoroughly extracted with acetone, and the combined sulfur was determined in the dried product. These experiments showed that with increasing quantities of sulfur (added at the beginning) and with increasing time of heating, the sulfur contents of the resulting products increased and approached values asymptotic to the value 32 per cent. These results were in complete harmony with those which Weber and Spence had obtained by a different method. The curves obtained for the course of vulcanization, however, were not as regular as had been expected.

[48] *Gummi-Ztg.*, **24**, 352 (1909). [49] *Kolloid-Z.*, **11**, 274 (1912). [50] *Ber.*, **46**, 1291 (1913).

Since it seemed probable that the proportionately large temperature fluctuations within the thermostat were responsible for the errors, new experiments were carried out by J. Wrück.[31] He used an oil thermostat, in which the fluctuation of temperature during the eight hours of the experiment was ± 5° C. The experiments were conducted at 170° C., using Ceylon plantation rubber, with vulcanization periods of 2, 4, 6, and 8 hours, and sulfur concentrations of 1 to 12 g. per 100 cc. of the pseudo-cumene solution of rubber. The experimental results are shown in Figure 52. The curves for the different periods of vulcanization

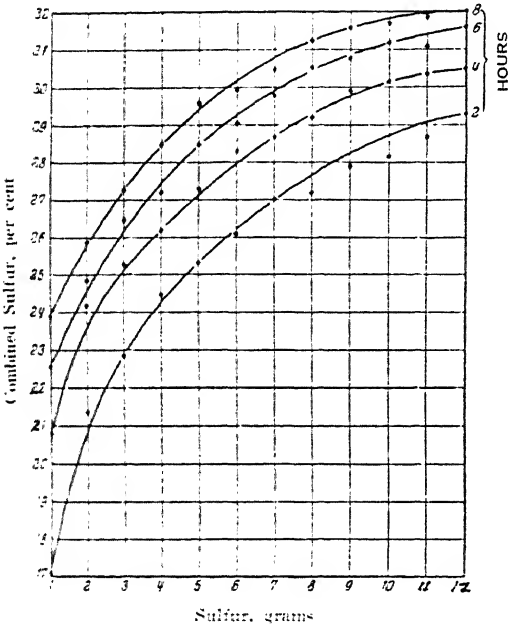


Figure 52—Hot vulcanization in solution.

show a fairly normal course, if slight irregularities are excluded. Obviously, the curves rise rapidly and approach a fixed end value, which lies at approximately 32 per cent combined sulfur in the curve for the sample vulcanized eight hours with the highest concentration of sulfur. This was not exceeded in any case, even with longer duration of vulcanization. The reaction product corresponding to the flattening of the curve evidently represents the final product of the interaction between rubber and sulfur, and therefore the highest possible degree of vulcanization. In the range of lower sulfur concentrations, the influence of the quantity of sulfur present on the rate of increase of combined sulfur is rather important, and the curves rise rapidly. The distance of the curves from one another for the different periods of vulcanization presents a further criterion for judging the course of vulcanization. The part of the sulfur was combined during the first stage of the heat-

[31] At the suggestion of Hinrichsen, Inaugural Dissertation, "Beitrage zur Theorie der Heissvulkanisation des Kautschuks," Dresden, 1915.

ing, as is shown by the time curves. The process advanced rather slowly, and at such a rate that from the end of the second hour to the end of the fourth, approximately as much sulfur was combined as was combined from the end of the fourth hour to the end of the eighth. The curve for the sample which was vulcanized for six hours lies almost halfway between the two neighboring curves.

In order to determine whether or not vulcanization is an addition reaction, Wrück investigated the behavior of the above vulcanizates with chloroform solution of bromine. He found that although the rubber samples which were in the lower degrees of vulcanization decolorized this solution approximately in proportion to the amount of sulfur which had combined with the rubber, the product containing 32 per cent combined sulfur no longer decolorized the bromine solution. In the last-mentioned case, therefore, all the double bonds of the rubber molecule are saturated with sulfur.

While Spence and Hinrichsen, with their co-workers, were successfully opposing the adsorption theory on an experimental basis, H. Loewen [52] sought to establish its untenability from a theoretical standpoint. After examining critically all the works of the older investigators cited by Ostwald, he came to the conclusion that no compelling argument for the conception of vulcanization as an adsorption phenomenon remained in existence, and that none of the observed phenomena presented any hindrances to the purely chemical conception of the process. He demonstrated particularly that, assuming the correctness of the earlier investigations, the adsorption equation $\frac{x}{a} = k \cdot c^m$ could not be applied to them, since all of the calculations are erroneous. It was his assumption that Ostwald had probably been misled by a typographical error.*

In a further investigation, Loewen [53] turned against the conception of Spence and Scott (*see* p. 285) that during vulcanization the adsorption of free sulfur is a step preceding chemical combination. He showed that, although the curves for the course of extraction of the free sulfur appear to be similar to adsorption curves, any real relation to adsorption curves is lacking. They merely show the progress of the addition of sulfur, as indicated by the results of the different extractions, without any relationship between the concentrations of sulfur at the beginning and at the end of vulcanization. From the same experimental data of Spence and Scott, Loewen constructed a curve showing the solubility of free sulfur in vulcanized rubber. This curve had nothing in common with an adsorption curve.

Loewen [54] then further investigated the solubility of sulfur in rubber. In a study of the literature, he discovered an observation of C. O. Weber,[55] recorded as follows: "Sulfur is usually heated about 20° above its melting point during vulcanization. It first forms small droplets of molten sulfur, which lie embedded in the mass of rubber and may easily be observed with a microscope during the earlier stages of vulcanization. These droplets disappear as the temperature rises and the vulcanization proceeds. Their disappearance may be partly due to the fact that the sulfur enters into combination with the rubber, but on the other hand, it also may be traced back to

[52] *Z. angew. Chem.*, **25**, 1553 (1912).

* Translator's Note. This conclusion has been the subject of some discussion by Ostwald [*Gummi-Ztg.*, **44**, 1743 (1930)] and Loewen [*Gummi-Ztg.*, **45**, 622 (1931)].

[53] *Z. angew. Chem.*, **25**, 1610 (1912).

[54] *Gummi-Ztg.*, **27**, 744, 923, 1301, 1647 (1913).

[55] *Gummi-Ztg.*, **18**, 83 (1903).

the fact that a simple solution of molten sulfur in the softened rubber hydro-carbon occurs."*

Weber apparently placed no great value upon the additional fact that strongly refracting droplets of sulfur separate in greater or less number upon cooling the rubber after it has been vulcanized in the presence of an excess of sulfur. His publications do not suffice, therefore, to demonstrate completely the solubility in question. His statements make plausible the observation that no more visible sulfur is found in hard rubber, even though considerable quantities can be extracted with acetone, a phenomenon which Weber [56] had noticed. Loewen undertook the task of determining, as exactly as possible, the solubility of sulfur in rubber. Like Weber, he used the microscope for this purpose, but he worked with dark field illumination. Vulcanization of the sample was accomplished between a slide and cover-glass in a laboratory drying oven at 130° to 140° C. If the sample was subjected to heat for only a short time, the microscopic image showed that the sulfur was melted and the preparation was filled with various sized droplets of sulfur. If the heating was continued further (20 to 30 minutes), the preparation appeared transparent. Upon cooling, more or less numerous droplets, of various sizes, separated from the supercooled sulfur, which had remained liquid below its solidifying point (114° C.). Undoubtedly, these droplets remain as such until spontaneous crystallization occurs, which almost always happens after some time. This phenomenon leads one to the assumption that sulfur is much more soluble in hot rubber than in cold rubber.

The following observations by Loewen show that the sulfur is dissolved in molecular form rather than in colloidal form. With long heating of the rubber in which the sulfur was dissolved, the free sulfur disappeared, and no further separation of sulfur occurred upon cooling the vulcanizate. In all probability, the "rubber sulfide" formed during vulcanization possesses a higher dissolving power for sulfur than the rubber itself, as is also suggested by the previously-mentioned behavior of hard rubber. Between the stage in which the droplets separate out and that in which the preparation remains completely clear, even when cold, there is a stage in which the rubber no longer contains enough free sulfur to be precipitated at proportionately higher temperatures, but in which it is still supersaturated with sulfur at a lower temperature. From such preparations, clear at first in the cold, the sulfur crystallizes in part in beautiful moss-like shapes. Furthermore, Loewen placed a piece of sulfur-free rubber between a slide and cover-glass and allowed molten sulfur to enter in such a way that, as a result of the capillarity in the intermediate space, it penetrated and enclosed the rubber droplet at its periphery. After heating the slide ¾ hour, he found that not only was the outer border of the rubber apparently vulcanized thoroughly, but also the sulfur was diffused, having apparently penetrated deeply into the interior of the rubber droplet, where it separated on cooling, first as small droplets, and then as crystals. Diffusion is, however, the important property which defi-

* Translator's Note. C. O. Weber seems to have been the first to employ the microscope in the study of the vulcanization process. A series of articles by P. Breuil [*Caoutchouc et gutta-percha* **2**, 82, 118, 158, 197 (1905)] represents an important early contribution to the subject. Loewen's work (1913) was followed by a microscopic study of the phenomenon of the "blooming" of sulfur by Regnaud [*Chimie and industrie*, **18**, 93 (1927)]. More recent microscopic experiments are reviewed on p. 646.
Refinements of microscopic technique recently applied to the observation of the vulcanization process by Dannenberg, Gee, Hock, Hünemörder, Miedel, and Walton, are described on p. 641.

[56] "The Chemistry of India Rubber," p. 112, Griffin and Company, London, 1909.

nitely differentiates true solutions from colloidal ones. The opinion of Spence and Scott, that adsorption of free sulfur plays a part in the beginning stages of vulcanization, hardly appeared plausible to Loewen, in view of these experiments. If one assumes that adsorption processes occur, the presence of an adsorbing surface must be presupposed. In a true solution, such surfaces are unthinkable. Therefore (since sulfur has been found to form a true solution in rubber), the idea of adsorption must be excluded from the consideration of the problem of vulcanization. According to Loewen, the explanation of the vulcanization process is as follows: the sulfur first melts, and then is dissolved in the rubber, in order to combine chemically with the latter in quantities which increase with the time of vulcanization.

Further experiments upon the solubility of sulfur in vulcanized and unvulcanized rubber were performed by H. Skellon.[57] Thin slabs of sulfur-free rubber and of unvulcanized rubber containing various amounts of sulfur were pressed together and heated for different intervals of time at the usual temperatures of vulcanization. The migration of sulfur from layer to layer was followed by analytical means. It was found that the sulfur did not migrate in all directions with equal speed. In a system of two adjacent layers of rubber an equilibrium of vulcanization is soon established, and the content of free sulfur in each layer definitely depends only upon the weight of rubber in the layer. The experimental procedure also made possible the approximate determination of the maximal solubility of sulfur, which was found to be about 10 per cent at the ordinary vulcanization temperatures (132° to 143° C.). These experiments also showed that sulfur dissolves in "rubber sulfide," and that its solubility in "rubber sulfide" is greater than in rubber itself. This observation offers a further explanation of the known fact that hard rubber can contain much greater quantities of free sulfur than can soft rubber, without the appearance of sulfur bloom. If it is assumed, in analogy to the behavior of other sulfide solutions, that polysulfides form in such solutions of sulfur in rubber sulfide, the observations made by various investigators that "after-vulcanization" proceeds more quickly in vulcanized than in any unvulcanized rubber, would be explained, since the sulfur produced by the decomposition of such polysulfides should be unusually active (*see* p. 283).

Venable and Greene[58] showed that the solubility of sulfur in rubber increases with the temperature and with the coefficient of vulcanization.* At values of combined sulfur greater than 7 per cent, no reliable data could be obtained, since migration of the sulfur was apparently retarded. It should be mentioned that Endres [*India Rubber World*, **68**, 635 (1923)], from the microscopic examination of films from evaporated cements, stated that the solubility of sulfur in rubber increased from 6.5 per cent at 95° C. to more than 10 per cent at 110° C. Kelly and Ayers [*Ind. Eng. Chem.*, **16**, 148 (1924)] applied Henry's law to rubber-sulfur mixtures and concluded that the first step in vulcanization is the solution (not adsorption) of sulfur by rubber. They found that the solubility of sulfur in rubber at 30° C. is about 1 per cent.

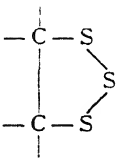
More recent microscopic observations by Loewen [*Kautschuk*, **4**, 243 (1928)] indicate that sulfur dissolves molecularly (probably as S_8) in the rubber, and he finds no evidence of "thio-ozone" or "thio-ozonides." By noting the temperature at which a thin film of rubber-sulfur mixture became clear upon heating, and the temperature at which it became cloudy upon cooling, Loewen determined that the solubility of liquid sulfur in raw rubber is 5 per cent at 53° C., 7.5 per cent at about 86° C., and 10 per cent at about 108° C.

Skellon reached somewhat different conclusions regarding the kinetics of vulcanization than did Spence, who studied mixtures of rubber with 10 per

[57] *Kolloid-Z.*, **14**, 96 (1914).
[58] C. S. Venable and C. D. Greene, *J. Ind. Eng. Chem.*, **14**, 319 (1922).
* Translator's Note.

cent of sulfur, and who thus was working with rubber which was saturated with sulfur at the start of the reaction. In this way, Spence did not encounter the formation of comparatively large quantities of rubber sulfide, which were able to influence the reaction through the formation of polysulfides. By the vulcanization of rubber mixtures containing 20 to 50 per cent of sulfur, Skellon readily obtained S-shaped curves, and concluded that polysulfides were formed as well as rubber sulfide. These polysulfides, he thought, accelerated the reaction of vulcanization by acting as sulfur carriers. This opinion was strengthened by the fact that in the calculation of combined sulfur based upon the amount of rubber sulfide present, discrepancies appeared which could not be accounted for by consideration of rubber resins, etc. Skellon accounted for the discrepancies by assuming the presence of polysulfides, which were not decomposed by boiling acetone at ordinary pressures. When these extracted residues were treated with acetone under pressure, a considerable additional quantity of sulfur could be extracted.

F. Kirchhof [59] experimented with the oxidation of vulcanizates at 100° C. in a current of air. He observed that one-third of the sulfur combined with the rubber was easily oxidized. It might be assumed that this portion of the sulfur was less firmly combined with the rubber, but it is improbable that there is an adsorption of sulfur which cannot be extracted from the vulcanizates by acetone. If such were the case, after the oxidation (which causes a thorough breaking up of the colloidal condition) this sulfur should be extractable by acetone and thus be detectable. However, this does not occur. If the total sulfur of vulcanization is considered to be chemically combined, and if it is considered that two-thirds of it remains in the oxidized product while one-third of it is removed by oxidation, then according to Kirchhof, one returns to the hypothesis already proposed by H. Erdmann (*see* p. 274), that an addition product of thio-ozone (S_3) to the hydrocarbon is involved in the vulcanization of rubber:



The atom of sulfur not directly combined with the rubber was considered to be the one which would be removed by oxidation.[60]

Kirchhof,[61] on the basis of later experiments, came to the following conclusions: The "depolymerization" effected by the heat during vulcanization accounts for the greater speed of reaction of the rubber colloid. In this condition, the more reactive sulfur, that is, the thio-ozone, acts to condense the rubber complexes. At the same time, there occurs a combination of a part of the sulfur. The latter occurrence is regarded as a necessary attendant phenomenon, rather than the specific cause of vulcanization. The condensing catalytic action of the sulfur (as thio-ozone) is more often regarded as the primary factor in vulcanization. From the standpoint of colloid chemistry, the change which the rubber undergoes in the addition reaction, and thus in

[59] *Kolloid-Z.*, **13**, 49 (1913).

[60] Bysow [*J. Russ. Phys. Chem. Soc.*, **53**, 79 (1921)], on the basis of experiments on the oxidation of vulcanizates with bromine water, came to the conclusion that sulfur was present in three forms: (1) acetone-soluble (2) oxidizable, and (3) neither extractable nor oxidizable.

[61] *Kolloid-Z.*, **14**, 43 (1914).

vulcanization, is as follows: From the state of least dispersion, in which the rubber exists in the cold, it goes by mechanical working, heat, or light, into a state of greater dispersion. Certain chemical elements and compounds behave in a quite analogous manner. The increase of reaction velocity, which accompanies the increasing degree of dispersion, finally leads to addition, or condensation, and thereby again to a state of less dispersion. Therefore, according to Kirchhof, hot vulcanization would produce a conversion of the colloidal state of the rubber (in which the molecular forces acting in various directions are limited) into a more vectorial state. The presence of molecularly dispersed elements or compounds therefore provides direction for the irregularly arranged forces of the colloid. Kirchhof sees in this conception a middle course between the purely chemical and the purely physical conceptions of vulcanization.

Although Kirchhof had already considered to some extent the physical-chemical conception of vulcanization, the whole question appeared in a new light through the experiments of C. Harries.[62] These experiments, which Harries conducted with the assistance of E. Fonrobert, were performed as follows: Para rubber was mixed with 10 per cent of flowers of sulfur, and vulcanized for 30 minutes at about 145° C. under a pressure of three atmospheres. The vulcanizates showed normal values for good Para rubber in the mechanical testing. If the mixture was stretched into the form of a thin sheet immediately after heating and was extracted for a long time with acetone, the test piece was found to have yielded nearly all of its sulfur to the acetone after 60 days.[63] Harries therefore concluded that ordinary vulcanization must be sharply differentiated from complete vulcanization, as the former is used in the production of many important soft rubber articles, and the latter finally leads to the production of hard rubber. According to his viewpoint, two reactions are to be considered in ordinary vulcanization: primary vulcanization and "after-vulcanization." The transformation of the first into the second stage takes place (he states) during prolonged storage in warm places, or in service. He further concluded from his experiments that the primary vulcanization was an adsorption reaction, and that the sulfur of the product of primary vulcanization did not go over into derivatives such as the hydrochloride. In contrast to this behavior, a vulcanized product which had undergone "after-vulcanization" yielded a hydrochloride which contained more or less sulfur. These conclusions agreed with the findings of Alexander and of Axelrod. Harries believed that natural rubber is in a metastable form, which is converted by primary vulcanization into another less reactive modification, the vulcanizate, or stable form. Hence, vulcanization should also be possible by the use of other materials (*see* p. 341). The transformation of the metastable form into the stable form is also accompanied by a change of chemical properties, for the hydrochloride of natural rubber is dissolved by chloroform, while the hydrochloride of desulfurized vulcanizates is completely insoluble in chloroform. The elementary composition of both is the same, but their decomposition products are different. The stable form is only difficultly attacked by ozone, and the solubility behavior of the two modifications is very different. It should be especially noted that the product of primary vulcanization extracted by acetone is not again subject to hot vulcanization, but produces blistered or brittle prod-

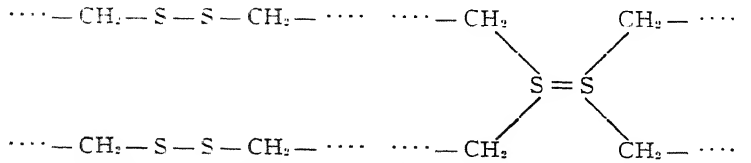
[62] *Kolloid-Z.*, **19**, 1 (1916); "Untersuchungen . . . . ," p. 104.

[63] According to Harries, these observations agree with results previously obtained by the chemists of the Continental company at Hanover.

ucts. Harries thought that this was due to the fact that only the metastable form of rubber is in the certain colloidal condition which adsorbs sulfur, whereby the vulcanization product obtains the tenacity and elasticity which are required for technical purposes.

H. P. Stevens [64] repeated the work of Harries and Fonrobert, and vulcanized mixtures of Para rubber and sulfur for 19 and 30 minutes at 145° C. The vulcanizates were extracted with acetone immediately after the heating process, and the extracted rubber was analyzed for combined sulfur after one, two, four, and nine weeks of acetone extraction. It was found that the sulfur content of the vulcanizate remained the same throughout the extraction. Stevens could not, therefore, confirm Harries' results. What circumstances resulted in the products which were so thoroughly examined and described by Harries are uncertain even today. Although Harries' idea of "primary vulcanization" and "after-vulcanization" is at least doubted today, it is interesting to note that there is an increasing tendency to consider the vulcanization process as consisting of two different simultaneous reactions. It is thought that the reaction involving the addition of sulfur to the double bonds of rubber predominates in the formation of hard rubber, but that in the formation of soft rubber, it is not the principal reaction.

The conclusions which Kirchhof [65] had reached in 1914 (*see* p. 292) led him to further experiments. A mixture of 100 parts of pale crepe rubber, 60 parts of [illegible], 1.5 parts of sulfur, 1 part of organic accelerator (*see* p. 316), and 7 parts of litharge was vulcanized by heating for 40 minutes at a steam pressure of 3 atm. The vulcanizate had the same superficial appearance and mechanical properties as though it were fully vulcanized, while a similar mixture which contained neither litharge nor magnesium oxide nor a larger quantity of organic accelerator as a substitute for litharge, was still typically under-vulcanized after 60 minutes' heating. Since the vulcanizate containing litharge was black, it apparently contained a considerable quantity of lead sulfide, and so only a small amount of sulfur could have combined with the rubber. Analysis showed 0.55 per cent of combined sulfur. Kirchhof therefore concluded that the litharge seemed to exert a specific effect in hot vulcanization in combination with organic accelerators, either the natural accelerators originally present in the rubber or those added to the mixture. How correctly Kirchhof estimated the relation will be seen in later chapters (*see* p. 309). In discussing the reactions which take place in hot vulcanization, Kirchhof expressed the opinion, which has often been repeated since then, that a "depolymerization" precedes vulcanization. If a cyclic structure be assigned to rubber, then it may be postulated that the first step of the vulcanization depends upon the reaction between sulfur and the free bonds of the terminal methylene groups appearing in the depolymerization of the ring molecule, together with a linking of two or more molecules:



If it is also assumed that sulfur, which consists of S_8 at its boiling point, has

[64] *J. Soc. Chem. Ind.*, **38**, 192T (1919). [65] F. Kirchhof, *Kolloid-Z.*, **26**, 168 (1920).

entered as such (with the help of partial valences) into reaction with the free bonds of the methylene groups according to the above formula, a gradual dissociation into S_2 molecules first occurs. This assumption could explain the remarkable results of Harries' experiments, for such sulfur can be extracted by solvents. Only at higher temperatures (above 130° C.) and higher concentrations of sulfur (over 10 per cent) can the rubber molecule add considerable quantities of sulfur to its double bonds. Such sulfur is no longer removable from the rubber molecule by physical means or by the ordinary chemical solvents for sulfur, without profound change of the rubber molecule. Therefore, according to Kirchhof, two kinds of "vulcanization sulfur" must be differentiated: a molecule (S_2 or S_8) bound to the end methylene group, which effects the condensation (vulcanization) of the depolymerized single molecule; and another, which apparently is added as atoms to the double bonds of the rubber hydrocarbon, and leads to hard rubber formation.

Van Iterson [66] pointed out that in constructing a theory of the vulcanization process, it must be borne in mind that ordinary sulfur ($S\lambda = S_8$) changes into other forms on heating. These could account for the combination of sulfur with rubber, and the velocity of the vulcanization process must be dependent upon these changes. However, Twiss and Thomas [67] later showed that under the usual technical conditions of vulcanization, $S\lambda$, the ordinary crystalline sulfur, and $S\mu$, the insoluble modification, which forms a part of the true flowers of sulfur, are practically identical in their action in vulcanization. Their vulcanizing action is apparently to be credited to the rapid conversion of $S\mu$ at the prevailing temperature into an equilibrium mixture, which is composed chiefly of $S\lambda$ with some $S\pi$, and in which the quantities of $S\pi$ increase noticeably if the temperature is raised to 140° C. or higher.

On the basis of calculations based upon the data of Twiss [*J. Soc. Chem. Ind.*, **36**, 782 (1917)] and Twiss and Brazier [*J. Soc. Chem. Ind.*, **39**, 125T (1920)], and upon certain data of Spence, Skellon, and others, Nordlander [*J. Phys. Chem.*, **34**, 1873 (1930)] has concluded that in both hot and cold vulcanization, the vulcanizing agent is activated amorphous sulfur ($S\mu$).* The mechanism of the process he believes to include the adsorption of sulfur on rubber and the chemical combination of activated $S\mu$ with rubber. For a further discussion of this theory, see Loewen, *Kautschuk*, **7**, 227 (1931); **8**, 15 (1932) and Nordlander, *Kautschuk*, **7**, 228 (1931); **8**, 13 (1932).

Dannenberg [*Kautschuk*, **3**, 104, 128 (1927)], as a result of observations with the ultramicroscope, has proposed the following explanation of the vulcanization process:

(1) Vulcanization is begun by the change $S\lambda \longrightarrow S\mu$ and the separation of colloidal $S\mu$.

(2) Accelerators are compounds which accelerate the change $S\lambda \longrightarrow S\mu$.

(3) Vulcanized rubber is a colloid system, in which raw rubber is the dispersing medium and $S\mu$ is the dispersed substance.

The Present State of Knowledge Concerning Vulcanization

Now that the investigations which are most important at present for an explanation of the mechanism of the vulcanization processes have been outlined, all the known facts concerning this topic may be summarized in the following statements.

Hot Vulcanization

1. Vulcanization takes place at any temperature. It proceeds continuously, either rapidly or slowly according to the experimental conditions, and normally

[66] *Verslag. Mededeel. Afdeel. Handel Dept. Landbouw*, **1916**, No. 2, Series 2; *Gummi-Ztg.*, **31**, 605 (1917).

[67] *J. Soc. Chem. Ind.*, **40**, 48T (1921).

* Translator's Note.

reaches its end point when a product which contains 32 per cent sulfur is obtained.

The minimum amount of sulfur required for the beginning of vulcanization was shown by Bruni [*Rev. gén. caoutchouc*, **8**, No. 75, 19 (1931); *Rubber Chem. Tech.*, **5**, 295 (1932)] to be 0.15 per cent, based on the rubber.* Results obtained by H. P. Stevens and W. H. Stevens [*J. Soc. Chem. Ind.*, **51**, 44T (1932)] agree with this value. The latter authors [*J. Soc. Chem. Ind.*, **48**, 55T (1929); **50**, 397T (1931)] have also found that the vulcanization coefficient may exceed 47, which is the value required by the formula C_5H_8S. They believed that the combined sulfur in excess of this value resulted from substitution, but that such a reaction took place only at temperatures above 70° to 100° C. and then only in the presence of a large excess of sulfur.

The temperature coefficient of the reaction velocity is from 2.6 to 2.8, and therefore lies within the limits considered applicable to chemical reactions.

Later work indicates that this value may be somewhat lower.* J. R. Sheppard [*India Rubber World*, **80**, No. 2, 56 (1929)] found a temperature coefficient of vulcanization of 2.59 for a litharge stock in the interval 242° to 332° F. (press cures). C. R. Park [*Ind. Eng. Chem.*, **22**, 1004 (1930)] obtained a value of 2.50 per 10° C. for a rubber-sulfur mixture. Park and Maxwell [*Ind. Eng. Chem.*, **24**, 148 (1932)] found that the average temperature coefficient for mixtures accelerated with 2-mercaptobenzothiazole was 1.91 and for mixtures accelerated with crotonaldehyde-aniline, 2.32 (judged by the physical properties of the vulcanizates). Using combined sulfur as a criterion, they obtained values of 2.30 and 2.67, respectively, for these stocks. Similar results have been observed by Sandstrom [*Ind. Eng. Chem.*, **25**, 684 (1933)] and by R. E. Morris [*Ind. Eng. Chem.*, **25**, 1400 (1933)] with stocks containing other accelerators.

Vulcanization is an additive process which depends upon the addition of sulfur to the double bonds of the rubber hydrocarbon. This is proved by the fact that hydrorubber (prepared by the method of Staudinger and Fritschi),[68] which no longer contains any double bonds, can no longer be vulcanized.

That vulcanization is to be treated as a chemical reaction also follows from the fact that sulfur-free rubber cannot be obtained again from vulcanizates, and that the combined sulfur passes over quantitatively into the product of the action of chlorine, bromine, nitrogen oxides, etc., upon the vulcanizates.

If vulcanized rubber is dissolved by treatment with solvents at high temperatures, and then the solvent is evaporated, there remains behind a soft sticky mass which possesses the same content of combined sulfur as the original sample. An entire change of the physical properties of the vulcanizate has thus occurred.

2. The reaction product of rubber and sulfur is always less soluble and less capable of swelling in the usual solvents for raw rubber, the more combined sulfur it contains. Relatively small quantities of combined sulfur suffice to change completely the behavior of rubber toward such liquids.[69]

Neither the fractionation of vulcanizates nor the vulcanization of raw rubber by the admixture of reclaimed rubber has ever been successful. This contradicts the assumption that solid solutions or adsorptions of sulfurized hydrocarbons in or on excess rubber are present in such vulcanizates. It must follow from this that in slightly vulcanized products all the rubber has been chemically combined with small amounts of sulfur.†

3. The mechanical properties of vulcanized rubber-sulfur mixtures depend upon the temperature of vulcanization and the duration of heating, and

* Translator's Note.

[68] *Helv. Chim. Acta*, **5**, 785 (1922).

[69] Cf. H. P. Stevens, *J. Soc. Chem. Ind.*, **38**, 195T (1919).

† Translator's Note. Using fractional peptization tests, Bacon [*J. Phys. Chem.*, **32**, 801 (1928)] found that rubber vulcanized with various amounts of sulfur remained homogeneous even when the combined sulfur content was less than 0.1 per cent.

are subject to manifold variations with increasing contents of combined sulfur. With soft rubber, however, a fixed amount of combined sulfur does not restrict the mechanical properties of the vulcanizate within fixed limits; in particular, the presence of a fixed amount of sulfur is not necessary to produce the optimum mechanical properties. The same quantity of combined sulfur in different samples of the same kind of rubber can result in completely different mechanical properties, if varying conditions of vulcanization are chosen.

4. Vulcanization with the aid of organic accelerators shows that the mechanical properties of soft rubber vulcanizates are better, the shorter the time and the lower the temperature which is necessary for the production of the optimum (for a given case) of these properties.* A much smaller quantity of combined sulfur is actually necessary for the attainment of this optimum cure when very powerful accelerators are used, and the mechanical properties of the vulcanizate are always better than when the vulcanization of a sample of the same rubber is conducted in the absence of the accelerator for a longer time and at a higher temperature.

5. If raw rubber is heated or masticated for a long time, it loses its "nerve" and becomes soft and plastic. If it is then vulcanized, proportionately slight quantities of combined sulfur suffice to change its physical properties considerably.

These facts are still insufficient to obtain the clearest insight into the whole complex question of vulcanization. They must rather be kept in mind, to be considered further in connection with points treated in detail in other chapters.

If the facts presented in paragraphs 1 to 5 are to be considered from a single viewpoint, the nature of raw rubber must be briefly reviewed.

As we have seen in earlier chapters, raw rubber, as it arrives for manufacturing, is anything but a chemically uniform substance. In addition to the rubber hydrocarbon, it contains the so-called rubber resins and proteins, substances which exercise a definite influence upon the rate of combination of sulfur with the rubber hydrocarbon, as will be seen in the sections which follow. Apart from these substances, however, a portion of the raw rubber consists of the rubber hydrocarbon, which is not a uniform, but a polyphase system, as Hauser and Pummerer were able to demonstrate. The latter investigator showed that the rubber hydrocarbon isolated from latex under certain conditions could be separated, by treatment with cold ether, into two fractions, the ether-soluble "sol-rubber," and the "gel-rubber" which is difficultly soluble in ether. Pummerer has also shown that this "gel-rubber" may become ether-soluble, by heating and mastication, for example, and that such a soluble "gel-rubber," when isolated from the solution, slowly changes again to the form which is difficultly soluble in ether. He interpreted this solubilizing of the "gel-rubber" as disaggregation, that is, as a destruction of the inter-molecular (apparently colloidal) arrangement of the original rubber molecules. The reverse process, i. e., the reversion to the ether-insoluble form of the stored disaggregated "gel-rubber," he designated as aggregation; that is, as the gradual formation of such an inter-molecular arrangement (*see* p. 175 and following).

* Translator's Note. N. A. Shepard and J. N. Street [*Ind. Eng. Chem.*, **24**, 574 (1932)] could observe no striking difference in the physical properties of various rubber compounds vulcanized at high and at low temperatures, although there seemed to be a trend toward better aging properties in the compounds vulcanized at low temperatures.

By considering these ideas of Pummerer together with the opinion of W. J. Kelly,[70] outlined below, one may obtain the following view of the present state of knowledge concerning the mechanism of the vulcanization process:

If raw rubber is heated and masticated, disaggregation occurs to a greater or less degree, according to the temperature and the method of treatment. To be sure, the so-called disaggregation must be considered together with a partial melting of the solid rubber substance, since rubber which has been made plastic upon hot rolls returns to somewhat near its original state relatively quickly. Now, if the action of sulfur in vulcanization were a surface phenomenon, it would be expected that the affinity of rubber for sulfur would change with increasing disaggregation, that is, with an increase in degree of dispersion and the resulting enlargement of the surface of the rubber. Similarly, it would be considered that if the action of heat and mastication should induce a depolymerization in a chemical sense, a larger effective rubber concentration would be present, since there would be more free, active double bonds present as a result of the depolymerization. Spence and Ward have shown, however, that under the same conditions of heating, the addition of sulfur to rubber does not take place more rapidly in rubber-sulfur mixtures which have been masticated for a long time on hot rolls than in slightly masticated mixtures.

The combination of sulfur with rubber during vulcanization appears to be a chemical reaction—an addition of sulfur to the double bonds of the rubber. It is known, furthermore, that isoprene molecules are grouped into the unit molecule of rubber in such a fashion that one double bond remains in each C_5H_8-group. No stopping point for the disintegration of the parent molecule by mastication or by normal hot vulcanization has been shown up to the present time. Moreover, since fractionation of the vulcanizates has not been successful, in the present state of knowledge it is necessary to assume that neither solid solutions nor adsorptions of sulfurized rubber are present in the slightly vulcanized products, but that all the rubber has been combined with a small amount of sulfur. Furthermore, one must assume that with continued vulcanization, more and more double bonds become saturated with sulfur, until the completely saturated product, containing 32 per cent sulfur, results. If this assumption were correct, one would, like C. O. Weber, expect to find a series of sulfur addition compounds, and the curves illustrating the course of the vulcanization would exhibit sharp breaks. This is known not to be the case. Rubber must not consist of unit molecules, therefore, but of aggregations of these. In addition, it is not homogeneous, but contains various phases of the same unit molecule (various units made up from the same unit molecule) in different degrees of aggregation. We should not, therefore, expect only one series of sulfur addition compounds to be formed during vulcanization, because every phase of the system will be enabled to form such a series, and the content of combined sulfur in each phase will change with the size of the aggregate. It is thus obvious that the curves illustrating the course of vulcanization will show no breaks, in spite of the existence of several such series of sulfur addition compounds, since the reactions proceed at the same time and mutually overlap each other. It happens that with continued heating, even during vulcanization, a disaggregation of the various phases will set in, and this complicates the conditions.

According to these ideas, we have to deal with a number of sulfur addition

[70] Bedford and Winkelmann, "Systematic Survey of Rubber Chemistry," p. 70, Chemical Catalog Co., Inc., New York, 1923.

products of various high degrees of aggregation, especially in the case of soft rubber. To be sure, it is assumed that these differ only very slightly in their physical properties, such as solubility, so that their separation is not feasible with the methods in general use today. Since the structure of rubber is not yet absolutely clear, however, these phenomena may be quite different. The preceding and following statements are not to be interpreted as a theory of vulcanization, but are merely to call attention to the gaps which must be filled in the knowledge of the process.

If a mixture of rubber and sulfur is heated, first the sulfur dissolves in the rubber, and afterwards the chemical reaction occurs. At the same time, the rubber is disaggregated under the influence of the heat.* This disaggregation proceeds together with the combination of the sulfur, and is influenced only by the rise of temperature and the method of heating. According to this conception, we have to deal with two processes which take place at the same time. On the one hand, there is disaggregation, which forms the depolymerized rubber and causes the rubber to become plastic, and on the other hand, there is the combination of sulfur, which improves the mechanical properties of the rubber.† In order to obtain a vulcanizate with good mechanical properties, we must, according to this working hypothesis, retard the disaggregation if possible, and at the same time promote the combination of sulfur with rubber in the most convenient way.

As we have already determined, the sulfur is first dissolved in the rubber by heating, in all probability as S_8. It cannot be added to the double bonds of the rubber molecule in this form, however, but must first be activated or changed to the atomic condition. This action is probably accomplished in part by the rubber hydrocarbon itself, but to a greater extent by the reaction of the sulfur with proteins and resins, as we will see in the following section. The rate of combination of sulfur with the rubber hydrocarbon depends upon the rate of formation of this "active" sulfur. If it forms slowly, the disaggregating action of the heat is made much more evident. If it is formed quickly, the combination of sulfur is promoted, disaggregation cannot exert its damaging action, and the result is a "nervy" product. The favorable action of organic accelerators upon the mechanical properties of the vulcanizate may be clearly explained upon the basis of these ideas. In the presence of accelerators, the "active" sulfur forms quickly, so that the combination of sulfur with the rubber takes place in a shorter time, and therefore at a final temperature lower than the normal vulcanization temperature (even at room temperature). The disaggregation is reduced to a minimum in this manner. We learn from the Peachey process (*see* p. 334), in which sulfur, formed in the nascent state from hydrogen sulfide and sulfur dioxide, causes vulcanization to take place almost instantaneously at room temperature, that the

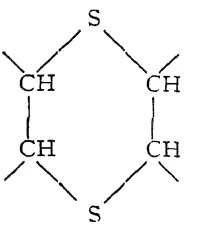
* Translator's Note. The effect of heat on the state of aggregation and the physical properties of rubber has been confirmed by Boiry [*Caoutchouc and gutta-percha*, **21**, 12257, 12293, 12335, 12386, 12454 (1924); **22**, 15507 (1925); *India Rubber J.*, **68**, 651, 687, 727, 771, 807 (1924)]. By the action of sulfur on rubber in solution, he obtained sols, gels, or precipitates of vulcanized rubber, depending upon the concentration of the solution and the nature of the solvent. More recent experiments concerning vulcanization in solution have been reported by Thiollet [*Rev. gén. caoutchouc*, **9**, No. 79, 5 (1932); *Rubber Chem. Tech.*, **5**, 296 (1932)] and Bourbon [*Rev. gén. caoutchouc*, **9**, No. 81, 9 (1932); *Rubber Chem. Tech.*, **5**, 630 (1932)].

† Translator's Note. Twiss [*India Rubber J.*, **65**, 607 (1923); *J. Soc. Chem. Ind.*, **44**, 106T (1925)] has advanced the idea that soft vulcanized rubber consists of an intimate mixture of particles of raw rubber and of the sulfide C_5H_8S (or C_5H_8SCl in cold vulcanization). The thought that the improvement in mechanical properties resulting from vulcanization may be caused by the reinforcing action of the rubber sulfide has received some support from H. P. Stevens and W. H. Stevens [*J. Soc. Chem. Ind.*, **51**, 44T (1932)].

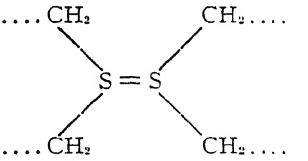
presence of "active" sulfur induces a rapid combination of sulfur with rubber.*

It is now to be assumed that the combination with sulfur has a stabilizing effect upon the rubber, and that disaggregation acts in the opposite manner. The following explanation can be found for this. It is known, to be sure, that sulfur adds to the double bonds of the rubber hydrocarbon and saturates them, but the manner in which this happens is still unknown. If one proceeds upon the hypothesis that the rubber hydrocarbon undergoes a disaggregation, but no change of constitution, during vulcanization, the following explanation would be plausible. One sulfur atom can saturate a double bond in one rubber aggregate (I); or two sulfur atoms can enter two double bonds in two different rubber aggregates, thus forming dithienes, with ring closures as in reaction (II), a process which is assumed to take place in the formation of factice.[71]

(I) $-CH=CH- + S \longrightarrow -CH(-S-)CH-$

(II) $-CH \quad S \quad CH- \longrightarrow$ 
$-CH \quad S \quad CH-$

If on the contrary one assumes, as did Kirchhof, after a study of the ring structure of the unit rubber molecule, that the ring becomes opened as a result of heating during vulcanization, so that CH_2-groups appear in the terminal positions, the linkage of two or more molecules by means of sulfur can happen in the following manner:

(III) $....CH_2-S-S-CH_2-....$ *or* 

Kirchhof assumed that saturation of the double bonds of the rubber which are not situated at the ends of the chains, leading to the formation of hard rubber, results only at higher temperatures and with higher concentration of sulfur. If saturation is assumed to occur as in Case I, the sulfurized rubber aggregates must be considerably more resistant to heating than the unvulcanized rubber. In Cases II and III, there is also an additional condensing action, so that disaggregation of the rubber by heat is equalized, at least in part, by condensation with the aid of sulfur.

If we now assume with Kelly that each rubber aggregate, regardless of its size, requires the addition of a fixed number of sulfur atoms in order to develop its optimum mechanical properties, and if we assume, for the sake of

* Translator's Note. P. Scholz [*Kautschuk*, **3**, 101, 127 (1927)], from freezing-point lowerings of sulfur when accelerators were added, concluded that accelerators affect the dynamic equilibrium between different forms of sulfur. They may accelerate the formation of the chemically active $S\pi$, or they may promote the formation of $S\mu$, which in turn may affect the colloidal structure of rubber or influence the polymerization of isoprene.

[71] Compare Henriques, *Z. angew. Chem.*, **8**, 691 (1895).

simplicity, that this fixed number should be two atoms, then the rubber would be unvulcanized if only one sulfur atom were added, and it would be over-vulcanized if three sulfur atoms combined with it. If the reaction which releases "active" sulfur progresses slowly, the disaggregation of the rubber particles is promoted, and a large number of smaller aggregates are formed. The rubber will then show a higher percentage content of sulfur in a normally vulcanized condition than if the action of the heat had been repressed by rapid activation of the sulfur. This conception would accordingly demand that a definite content of combined sulfur should be necessary for the saturation of each degree of aggregation, that is for each particle size of the rubber, if the best mechanical properties are to be obtained. If, when this content has been reached, the heating is continued in the presence of free sulfur, vulcanization continues, and this leads to over-vulcanization. If, on the contrary, no more free sulfur is present and the heating is continued, the rubber particles split into smaller aggregates. These aggregates no longer have the sulfur content which is necessary for the attainment of their optimum mechanical properties, and therefore they are under-vulcanized.

The course of vulcanization is usually observed experimentally by determinations of combined sulfur content, tensile strength, or resistance to aging.* B. S. Garvey, Jr., and W. D. White [*Ind. Eng. Chem.*, **25**, 1042 (1933)] have found no test which is satisfactory for independent use as a measure of the degree of vulcanization. They employ a group of tests for this purpose, using measurements of plasticity, hysteresis, and stress-strain relations, with limiting values for vulcanized and unvulcanized rubber.

A physical test, called the "T-50 Test," has been proposed by W. A. Gibbons, R. H. Gerke, and H. C. Tingey [*Ind. Eng. Chem., Anal. Ed.*, **5**, 279 (1933)] to determine the state of vulcanization (see the translator's note on p. 552).

The possibility of demonstrating the course of vulcanization by means of fluorescent effects obtained upon exposing samples to filtered ultra-violet light is discussed in the translator's note on p. 643.

The reactions which occur during the so-called reclaiming of vulcanized rubber (*see* p. 342) can also be explained more clearly according to these ideas. Reclaiming will be treated hereafter only as a disaggregation of vulcanized rubber particles, in the course of which a normally vulcanized starting material is changed into the under-vulcanized condition, so that a normally vulcanized product can again be obtained by means of further vulcanization of the reclaimed rubber, after mixing it with elementary sulfur. The reclaiming process shows clearly, however, that heat must exert less disaggregating action on vulcanized than on unvulcanized rubber. It seems correct to assume that the combination of sulfur with the rubber during the process of vulcanization protects the rubber from complete decomposition.

If we add a powerful accelerator (a material which causes the formation of active sulfur to take place more rapidly and at lower temperatures than are usual during the course of vulcanization) to a rubber-sulfur mixture, the disaggregating influence of the heat becomes of only slight importance. Some large rubber aggregates remain; these require a smaller content of sulfur than the smaller aggregates for producing their optimum physical properties. According to these views, the rate of combination of sulfur with the rubber aggregate is the decisive factor during the vulcanization process, since it counteracts the disaggregating action of heat. The faster the addition of sulfur takes place, and the lower the temperature required for vulcanization, the smaller is the amount of disaggregation which occurs, and the greater is the "nerve" of the vulcanizate.

*Translator's Note.

An extensive chemical theory of vulcanization has been announced by Boggs and Blake [*Ind. Eng. Chem.*, **22**, 744, 748 (1930)].* For a review of the earlier investigations which are related to the new theory, see Nuttall and Kirkwood [*India Rubber J.*, **80**, 657 (1930)] and pp. 461, 469, 470.

According to Boggs and Blake, there are two separate and successive chemical reactions involved in the vulcanization of rubber with sulfur. The formation of soft rubber consists in the addition of sulfur to the more reactive terminal double bonds of the rubber hydrocarbon, with no heat effect. After the soft rubber reaction has been completed, the formation of hard rubber may proceed by the progressive addition of sulfur to the internal double bonds from one end of the rubber molecule to the other. The hard rubber reaction was found to be exothermic and of the second order.

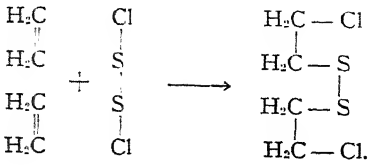
Experiments conducted by B. S. Garvey, Jr., and W. D. White [*Ind. Eng. Chem.*, **25**, 1293 (1933)] have led them to conclude that in vulcanization the sulfur may act (1) directly by addition and (2) as a catalyst for a reaction at the double bond of the hydrocarbon which does not change its unsaturation. Vulcanization to produce ordinary soft rubber involves both reactions, they believe, although in high accelerator—low sulfur compounds, the sulfur acts primarily as a catalyst. The addition reaction is considered to be the principal reaction in the vulcanization of hard rubber.

Lindmayer [*Kautschuk*, **5**, 35 (1929); *India Rubber J.*, **82**, 218, 249 (1931)] has recently proposed an explanation of the vulcanization process based on three-dimensional structures.

Cold Vulcanization

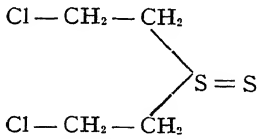
In general, the theories formulated for cold vulcanization are similar to those which were advanced for hot vulcanization. Naturally the disaggregating effect of heat is excluded. In its place, however, we must consider the process of dissolving rubber, the influence of which is much the same as that of heat, under technical conditions. In the manufacture of articles vulcanized in the cold, the rubber is usually first converted into a solution, then the object is formed, and finally vulcanization follows. The processes of disaggregation and combination of sulfur, which proceed simultaneously during hot vulcanization, are temporarily separated during cold vulcanization. Sulfur chloride takes the place of sulfur as a vulcanizing agent.

It can easily be shown that the combination of sulfur chloride with the rubber is to be treated as a chemical combination, and not as an adsorption phenomenon. Rubber samples vulcanized without heat are not affected by the action of water, while if the sulfur chloride were adsorbed as such, an evolution of hydrogen chloride, hydrogen sulfide, and sulfurous acid would be expected under such circumstances. It must, therefore, be assumed that the sulfur chloride adds to the double bonds of the rubber molecule. Kelly (*see* p. 298) has recently called attention to the fact that apparently these reactions are actually much more complicated in nature than it has generally been assumed. It was formerly believed that sulfur chloride added to ethylene and similar unsaturated compounds, and likewise to rubber, in the following manner:



Observations on similar products made from mustard gas make the following formula seem more probable, however:

* Translator's Note.



It has now been established without question by various authors that cold vulcanization has been completed when the rubber has taken up half its weight of sulfur chloride. The compound formed was assigned the formula $(C_{10}H_{16})_2S_2Cl_2$, in accordance with the ideas concerning the constitution of the rubber molecule at that time. According to the present status of our knowledge, however, the conception of the parent molecule of rubber as $C_{10}H_{16}$ is not correct, since it is now believed that there are at least eight isoprene groups and therefore eight double bonds contained in the unit molecule. Such a unit molecule would, therefore, unite with two molecules of sulfur chloride, according to the formula given above for the sulfur chloride addition product, but these two molecules of sulfur chloride could saturate only four of the eight double bonds which are present.

In the final product of cold vulcanization, a highly unsaturated compound must therefore be present. Now if this unsaturated compound could, like mustard gas, split off the sulfur atom which is connected to sulfur (*see* the above formula), and if it were as powerful as sulfur in the nascent state, it would saturate more double bonds. Since two molecules of sulfur chloride are added to each unit molecule, in each molecule of rubber there would be present two sulfur atoms which could split off and saturate two more double bonds. According to this assumption, two double bonds always remain unsaturated in the final product of cold vulcanization of the unit rubber molecule. It is evident from this presentation of the subject, that the whole question of the addition of sulfur chloride to the rubber molecule is in urgent need of further investigation. It might also be suggested in this connection, that the chlorine may be split off practically quantitatively, in the form of hydrogen chloride, from the final product of the reaction of the purest rubber hydrocarbon with sulfur chloride, by boiling it with alcohol. This phenomenon, when considered in connection with the properties of the resulting product, is quite remarkable.

It should be sufficiently apparent from all this, how small the knowledge concerning the mechanism of the vulcanization process is at the present time. Certain hypotheses may be drawn from the known facts, but until the problem of the structure of rubber is solved, no completely satisfactory answer to the question can be given. Hence the studies on the structure of rubber recently undertaken by the German chemists (*cf.* the section on the "Chemistry of Rubber") are of special importance. The acknowledged progress of these investigations leads us to hope that in the near future we may succeed in penetrating the veil of darkness which today surrounds the problem of vulcanization, by concentrated attack on this problem with the most modern methods of research.

Substances Influencing Vulcanization

The Effect of Natural Non-Rubber Constituents of Rubber

As pointed out in a previous section (*see* p. 160 ff.) crude rubber as it is received at the factory contains so-called resins and protein matter, in addition to the rubber hydrocarbon. Since various types of rubber prepared from the same botanical source by different methods may differ in their capacity

for vulcanization, it may be surmised that these impurities are capable of influencing the reaction of sulfur with the rubber hydrocarbon. C. O. Weber[72] noticed that Mangabeira rubber and certain African rubbers would not vulcanize in hot air, with small amounts of sulfur even in the presence of the powerful accelerator, litharge, while other varieties such as Para, vulcanized readily. He established,[73] furthermore, that the sulfur reacts with the resins at vulcanization temperatures, the sulfurized resins being soluble in acetone. However, the question as to whether the naturally occurring impurities of rubber accelerate or retard vulcanization, was really first considered in a lecture by Lothar E. Weber.[74] He believed that the poor vulcanization of low grade rubbers of high resin content (about 20 per cent) as mentioned above was to be explained by the fact that the amount of sulfur available for vulcanization was greatly reduced by the reaction of some of the sulfur with the resins of the rubber at vulcanization temperatures.

The more nearly resin-free a rubber is, the more satisfactory it may be expected to be in vulcanizing properties. However, from his investigations of Highland sheet rubber, he concluded that the resin plays an active part in the vulcanization, indeed that its presence may be absolutely essential, for the resin-free rubber did not vulcanize. That this is not exactly the case, however, may be concluded from the previously described investigations of Spence and Young,[75] which were carried out at 50° to 75° C. In a mixture which contained only the purest, resin-free rubber and 10 per cent of sulfur, vulcanization took place at 75° C., though so slowly that after 90 days the percentage of combined sulfur was only 0.32 per cent. This gradually increasing amount of sulfur, not removable with acetone, was taken as evidence of a slow vulcanization under these conditions. On the other hand, a second mixture containing 10 per cent sulfur and 1 per cent of the acetone extract of the raw rubber, i.e. the resin, showed 9.36 per cent of the sulfur to have been taken up by the rubber hydrocarbon in the same length of time at the same temperature. L. E. Weber's conclusion that the resins are concerned in vulcanization appeared to be confirmed. C. Beadle and H. Stevens[76] arrived at entirely different results in their investigations of the influence of the resins of raw rubber on vulcanization. Sheet rubber (not smoked) from the Malayan Peninsula, of average color and containing 2.5 per cent of resins, was deresinated by extraction with acetone. To the extracted rubber were added in one case 2.5 per cent of the resin extract, in another 2.5 per cent of jelutong resin (*see* pp. 39 and 138), and in a third, colophony. Seven per cent (7 per cent) of sulfur was added to each mixture and the compounds were vulcanized in the usual manner. Chemical analysis of the vulcanizates showed the vulcanization coefficients recorded in Table 4, based on resin- and protein-free rubber.

TABLE 4.—*Influence of Resins on Vulcanization.*

Material	Vulcanization Coefficient
Original resin-containing rubber	2.86
Resin-free rubber	2.71
Resin-free rubber plus 2.5 per cent acetone extract	3.12
Resin-free rubber plus 2.5 per cent jelutong resin	2.58
Resin-free rubber plus 2.5 per cent colophony	2.85

[72] *Gummi-Ztg.*, **19**, 272 (1904).
[73] *Gummi-Ztg.*, **16**, 931 (1902); **17**, 898 (1903); **19**, 83 (1904).
[74] *Orig. Comm. Eighth International Congress of Applied Chem.*, **9**, 95 (1912).
[75] *Kolloid-Z.*, **13**, 265 (1913); *cf.* p. 284.
[76] *Kolloid-Z.*, **11**, 61 (1912); **12**, 46 (1913); **14**, 91 (1914); *Orig. Comm. Eighth International Congress of Applied Chem.*, **9**, 581 (1912).

As far as effect on chemical vulcanization is concerned, the resins did not appear essential in this experiment. Beadle and Stevens observed, however, that the resin-free vulcanizate and those containing jelutong or colophony aged rapidly, and became hard and brittle. Thus the natural resins of rubber act also as powerful antioxidants. In connection with these investigations, Beadle and Stevens studied the influence of nitrogen-containing impurities, the proteins, on the vulcanizing properties of the same rubber. The rubber was swollen in benzene and the lower part of the solution, which contained the whole of the insoluble nitrogenous part, was separated. After evaporation of the solvent from both portions of the solution, two fractions were obtained, the one high in nitrogenous constituents, the other nitrogen-free. Portions of each were extracted with acetone to study the effect of resins and proteins together. Vulcanizates prepared in the usual manner with 7 per cent of sulfur gave the analytical results in Table 5.

TABLE 5.—*Influence of the Proteins on Vulcanization.*

Material	Vulcanization Coefficient
Untreated rubber	2.86
Protein-free rubber	1.15
Protein- and resin-free rubber	1.08
Rubber with an excess of protein	3.62
Resin-free rubber with an excess of protein	3.34

Here again the resins appear to have little effect, while the nitrogenous substances act as powerful sulfur carriers.[76a]

In this connection, the very interesting investigations of Stevens which deal with the possibility of replacing the nitrogenous impurities of rubber with other substances, might be discussed briefly. For this purpose, the protein-free rubber was mixed with peptone (Riedel), casein, starch, or litharge, and 7 per cent of sulfur and vulcanized in the usual manner. (*See* Table 6.)

TABLE 6.—*Influence of Proteins, Starch, and Litharge on Vulcanization.*

Material	Vulcanization Coefficient
Protein-free rubber	1.15
Protein-free rubber plus 3 per cent peptone	3.22
Protein-free rubber plus 3 per cent casein	1.76
Protein-free rubber plus 3 per cent starch	1.42
Protein-free rubber plus 10 per cent litharge	3.02

As seen in the table, peptone can replace the natural nitrogenous constituents of rubber, but other nitrogen-containing organic compounds, such as casein, do not function similarly to peptone. Nitrogen-free substances such as starch also exert a definite effect on the process of vulcanization. The experiment with litharge was most interesting, and more will be said later concerning it.

The influence of resins on the course of vulcanization has been studied by J. Wrück.[77] As in his previous work, he heated 2 per cent solutions of resin-containing or of resin-free Ceylon plantation crepe in pseudocumene, with 12 grams of sulfur at 160° C. ± 5° C. Test pieces taken after various periods of vulcanization were carefully freed from excess sulfur and analyzed for combined sulfur. The vulcanization curves led to the conclusion, "that the resins act as weak positive catalysts of vulcanization." Although these results agreed with those of Beadle and Stevens, Wrück considered it not impossible that resins of other kinds of rubber might bring about other vul-

[76a] *See* L. Eck, *Kautschuk*, **7**, 206 (1931).

[77] Dissertation, Dresden **(1915)**. *See* p. 288.

canization phenomena. The correctness of this consideration was confirmed by later work, especially by the investigations of G. Martin and F. L. Elliot[78] on the influence of the kind and amount of the natural non-rubber constituents of rubber on the content of combined sulfur of the vulcanizates. They used in their investigations 24 rubber samples, of which six were crepe and six were sheet rubbers of both ten and twenty year old trees from the same plantation. Since the average composition of these samples is of interest in other connections, the data are given in Table 7.

TABLE 7.—*Influence of the Naturally Occurring Non-Rubber Constituents of Rubber on Vulcanization.*

	Type	Resin Per cent	Protein Per cent	Ash Per cent	Rubber Per cent	Vulcanization coefficient
10 Year Old Trees	Sheet	1.98	2.27	0.28	95.47	5.47 ±0.1
10 Year Old Trees	Crepe	2.86	2.25	0.28	94.61	5.20 ±0.1
20 Year Old Trees	Sheet	1.73	2.09	0.28	95.90	5.38 ±0.1
20 Year Old Trees	Crepe	2.65	2.11	0.25	94.99	5.00 ±0.0

All of the mixtures contained ten per cent of sulfur, and the cure was chosen so that the vulcanizates required the same load to stretch them to the same elongation (standard vulcanization). From the table it may be seen that the average vulcanization coefficient of the crepes was distinctly less than that of sheets from trees of the same age, although the protein content of both kinds was practically identical and the resin content of the crepes lay considerably above that of the sheets. According to these results, crepes vulcanize slower than sheets. This conclusion agrees with the experimental results of Schidrowitz and Goldsbrough,[79] as well as with those of O. de Vries and W. Spoon.[80] The age of the trees also seems to have a slight effect on the vulcanization of rubber obtained therefrom.[81] As is shown in the accompanying table and directly demonstrated by the experiments of Martin and Elliot, it is not the amount of accessory constituents in the rubber which plays the decisive part in its ease of vulcanization. On the contrary, it is primarily the variability of the nature of the rubber with the method of preparation which is important, that is, the treatment of the coagulum for the manufacture of the various trade varieties of rubber. When identical samples of normal crepe rubber were mixed with 10 per cent of sulfur and 2 per cent of acetone extract of crepe, sheets, or slab rubber (*see* p. 119) and vulcanized 115 minutes, the analyses in Table 8 were obtained.

TABLE 8.—*Influence of Various Rubber Resins on Vulcanization.*

Materials	Combined Sulfur Per cent	Vulcanization Coefficient at the Standard Vulcanization
Crepe	3.24	4.2
Crepe plus crepe resin	3.45	4.6
Crepe plus sheet resin	4.45	5.4
Crepe plus slab resin	6.20	5.3

In agreement with the experimental results of Stevens and of Wrück, the resin of crepe rubber is shown here to have actually only a slight influence on the course of vulcanization. The acetone extracts of sheets and slab rubber, however, serve as powerful accelerators. As much work, mostly in the rubber growing regions, has shown, the influence of the method of preparation of the coagulum is so great that other factors such as, for example, the age of

[78] *J. Soc. Chem. Ind.*, **41**, 225 (1922).

[79] *India Rubber J.*, **54**, 162, 184 (1917).

[80] *Arch. Rubbercultuur*, **3**, 246 (1919).

[81] *Cf.* O. de Vries, *Arch. Rubbercultuur*, 1, 169 (1917).

trees, the dilution of latex,[82] the method of coagulation,[83 84] etc., are relatively unimportant. An explanation of the behavior of the various forms of the coagulum from Hevea latex, may be found in the differences in the various methods of handling it (*see* p. 108 ff.). In the preparation of sheets, the wet coagulum is merely pressed between rolls and then dried. There remains in the rubber, therefore, a part of the serum substances which were present in the coagulum after coagulation. In the preparation of crepe, however, the rubber is washed between rolls under a stream of water and is thereby much more thoroughly freed from serum constituents. Thus there must be a substance contained in the watery portion of latex, which promotes vulcanization. Eaton and Grantham [85] were able to prove this, and thus to explain the fact, that rubber obtained by the evaporation of latex, containing all the serum constituents, always vulcanizes rapidly. According to H. P. Stevens,[86] this property is not lost when such rubber is extracted with water or acetone.

In addition to the accelerating substances already existing in latex, another natural accelerator is formed if the wet coagulum is not worked into sheets at once, but is allowed to remain many days at the temperature of the tropics, as is the case in the preparation of slab rubber. During this maturing of the coagulum, a process of putrefaction of the proteins contained in the serum proceeds under the influence of bacteria or fungi, yielding vulcanization accelerators (*see* p. 101). Eaton has isolated these basic decomposition products by painstaking work and has shown that addition of these substances to ordinary rubber produces a corresponding acceleration of vulcanization. The high rate of vulcanization of a matured coagulum is also retained if it is later creped. Thus the active principle formed by maturation cannot be washed out with water. If the fresh coagulum is heated or treated with antiseptic substances, the maturation process does not take place. This is, of course, striking proof that maturation is caused by the presence of lower organisms. The smoking of rubber has an antiseptic effect, on account of the phenolic constituents contained in the smoke.[87] This explains the fact that smoked sheets cannot be vulcanized as rapidly as unsmoked sheets. The high rate of vulcanization of unsmoked sheets indicates that maturation takes place during drying, though to a lesser extent than in slab rubber. Occasionally this is directly recognized through the so-called "rust" formation (*see* p. 148). The serum constituents, present in relatively large quantities in the sheets, in the case of rust formation, decompose, especially at the surface, forming a slimy coating which later dries to a film. If such rubber is stretched, the brittle film cracks into many pieces, which cover the surface of the rubber much as rust covers iron.

G. Bruni and T. G. Levi [88] have undertaken the laborious task of investigating the composition of the acetone extract of matured rubber. They established once again, that the acetone-soluble constituents decidedly influence the rate of vulcanization of slab rubber, since the rubber when freed from these constituents has a markedly diminished capacity for being vul-

[82] Eaton, *Dept. of Agriculture, Federated Malay States, Bull.* **No. 17,** 23 (1912); Spoon and de Vries, *Arch. Rubbercultuur,* **5,** 115, 294 (1921).

[83] de Vries, *Arch. Rubbercultuur,* **1,** 40 (1917); **4,** 210 (1920). Eaton, *Dept. of Agriculture, Federated Malay States, Bull.,* **No. 27,** 207, 222; *Bull. Imp. Inst.,* **20,** 454 (1922). Stevens, *Bull. Rubber Growers' Assoc.,* **2,** 142 (1920); **4,** 137 (1922).

[84] O. de Vries, "Estate Rubber."

[85] *J. Soc. Chem. Ind.,* **34,** 989 (1915); **35,** 715 (1916); Eaton, Grantham and Day, *Dept. of Agriculture, Federated Malay States, Bull.,* **No. 27,** 78 (1918). *Cf.* also Spence, *J. Ind. Eng. Chem.,* **10,** 115 (1918).

[86] *J. Soc. Chem. Ind.,* **41,** 326 (1922).

[87] *Cf* **35,** 715 (1916).

[88] *Giorn. chim. ind. applicata,* **7,** 447 (1925); **9,** 161 (1927).

canized. The acetone extract can be separated into ether-soluble and water-soluble portions. The former consists chiefly of higher fatty acids; the latter contains the natural nitrogenous constituents. The water-soluble portion was evaporated after being decolorized with animal charcoal. A quantity of alpha-aminovaleric and alpha-aminocaproic acids, amounting to approximately 10 per cent of the water-soluble part, separated. These amino acids, which can also be isolated from smoked sheets, did not accelerate vulcanization very noticeably. From the solution remaining, phenylacetic acid in the form of its silver salt could be precipitated with silver nitrate. Further investigation showed that this acid was probably present as its potassium salt in the slabs, and amounted to approximately 30 per cent of the water-soluble portion of the acetone extract. It was also shown that this salt, like the potassium salts of the fatty acids, behaved as a vulcanization accelerator. Finally, Bruni and Levi found in the water-soluble portion of the acetone extract some 20 per cent of a mixture of tetra- and penta-methylenediamines, both of which accelerate vulcanization powerfully. In the ordinary kinds of rubber these bases could not be found, so that they appear to be characteristic of slab rubber. From the ether-soluble portion of the acetone extract, phytosterin, which is without action on vulcanization, was isolated. The ether extract did not contain bases. These investigations of Bruni and Levi show clearly that not so much the amount, but the nature of the nitrogenous constituents present in the rubber, is important. Thus, slab rubber, which vulcanizes especially rapidly, ordinarily contains less nitrogen than rubber prepared by other methods. Some of the decomposition products of the nitrogenous substances originally contained in the rubber are volatile and soluble in water. The largest loss of nitrogen-containing compounds occurs in the preparation of crepe rubber from slab rubber, but this loss is decreased if the slab rubber is first smoked.

Although this maturation process explains the high rate of vulcanization of slab rubber and, to a certain extent, the behavior of dried unsmoked sheets, it can not be offered as an explanation for the marked difference in vulcanization of crepe and smoked sheets, especially in early years, for we have seen that the decomposition of proteins is checked by smoking. The amount of nitrogen-containing constituents alone cannot be decisive, for Martin and Elliot (*see* p. 306) have shown that various kinds of rubber may possess different rates of vulcanization in spite of identical protein contents. G. S. Whitby and A. R. Winn,[89] who have carefully studied these phenomena, believe that the solution of the question lies in the varying acid content of the acetone extract of the various kinds of rubber. If these are extracted with acetone, and the acetone extract after distillation of the solvent is taken up with warm neutral alcohol and then titrated (using phenolphthalein as an indicator), the "acid numbers" as shown in Table 9 result, based on 100 grams of rubber and expressed in mg. of potassium hydroxide required for neutralization.

These data indicate that even the same method of preparation produces rubbers with considerably different acid contents of the acetone extract.[90] The amount of resin in the rubber is, therefore, not proportional to the acid number of the acetone extract. Since this subject will be discussed later, in the chapter on vulcanization accelerators, a statement of the facts only, will be

[89] *J. Soc. Chem. Ind.*, **42**, 336 (1923).

[90] *Cf.* O. de Vries, "Estate Rubber . . . ." pp. 613, 618.

TABLE 9.—*Acidity of Various Kinds of Rubber.*

Rubber	Acetone Extract Per cent	Acid Number
Sprayed rubber (creped)	4.85	390
Light brown crepe	3.00	320
Sprayed rubber (slabs)	4.00	301
Light latex crepe	3.02	296
Light latex crepe	3.01	289
Smoked Sheets	3.25	289
Smoked Sheets	2.82	284
Dark Smoked Sheets	3.37	283
Smoked Sheets	3.15	283
Smoked Sheets	3.35	280
Smoked Sheets	3.13	276
Smoked Sheets	3.05	270
Smoked Sheets (milled on hot rolls)	2.22	239
Smoked Sheets	3.33	236
Slab crepe	2.44	224
Brown crepe (second sub-grade)	2.74	223
Slab, gray-brown crepe	1.79	139
Slab, dark-brown crepe	1.77	92

given here, without touching upon the conclusions which result from them, especially the conclusions resulting from experiments with pigmented mixings. The observations of Bruni and Levi [91] have shown that matured rubber is distinguished from other rubbers by a considerably higher acid content, and that this acid may be removed by washing or by vacuum drying at 130° C., without altering the rate of vulcanization. Thus it may be seen that the variation in behavior of various rubbers in rubber-sulfur mixtures may be due to a number of causes. In the table we see also that creped slab rubber shows a comparatively low acid number. In this connection it may be of interest to note that Bruni and Levi could identify acetic and valeric acids in the distillation products of matured rubber, and that, according to them, these acids were present originally in the rubber as ammonium salts or amides.

In conclusion, the changes which can take place in the vulcanizing capacity of the stored finished product may be briefly discussed. In general, the high quality rubbers may be stored several years without their quality being affected. Stevens,[92] and de Vries [93] were able to show, however, that storage tends to equalize the different rates of cure. Rapidly-vulcanizing rubbers later vulcanize more slowly and slowly-vulcanizing rubbers after storage for a long time vulcanize somewhat faster. Certain surface defects such as, for example, mold formation on dried sheets, which usually do not influence the quality of the rubber, may alter the rate of vulcanization, if the defect occurs in the rubber to a great extent. Thus the gray-green mold which develops in daylight retards vulcanization, while the black and yellow pinhead types which develop in the dark slightly accelerate the vulcanization.

THE ACTION OF VULCANIZATION ACCELERATORS

Inorganic Accelerators

It has long been known that the hot vulcanization of rubber is accelerated by certain inorganic substances, such as lime, magnesia, lead compounds,[94] etc. For example, addition of a large amount of litharge to a rubber-sulfur mix,

[91] *Giorn. chim. ind. applicata*, **7**, 447 (1925).
[92] *J. Soc. Chem. Ind.*, **37**, 340 (1918). *Bull. Rubber Growers' Assoc.*, **3**, 190, 243, 280, 472 (1921); **4**, 331 (1922).
[93] *Arch. Rubbercultuur*, **5**, 140 (1921).
[94] Charles Goodyear, the discoverer of vulcanization, used white lead as a pigment in rubber-sulfur mixtures.

under certain conditions may decrease the time of vulcanization to less than one-half the normal period. Such a mixture darkens progressively with the course of vulcanization, as a result of the formation of lead sulfide.

C. O. Weber attributed the accelerating action of these materials to their basic character. This was shown not to be the controlling factor by K. Gottlob,[95] since the strongly alkaline oxides of barium and strontium did not exert a similar action. E. Seidl[96] found that equal percentages of zinc oxide and lead oxide (23 per cent) resulted in different coefficients of vulcanization when used in a given rubber-sulfur mixture. While the zinc oxide compound contained 1.66 per cent combined sulfur, the lead oxide compound contained 2.93 per cent of combined sulfur. These two oxides therefore function differently. The earlier writers attributed the acceleration which occurs with litharge to its high heat conductivity. Under similar conditions, therefore, the time of vulcanization of a rubber compound should be inversely proportional to the heat of conductivity of the inorganic material in the compound, that is the larger the heat conductivity, the smaller should be the time required to attain a definite coefficient of vulcanization. Seidl demonstrated that litharge and zinc oxide possess approximately the same heat conductivity. He showed also that a sulfur-free litharge-rubber mixture possesses approximately the same heat conductivity as a similar zinc oxide-rubber mixture (the weight of the pigments was the same in each compound). It was demonstrated that a compound consisting of aluminum bronze and rubber was a better conductor of heat than either one of the above mentioned compounds. Therefore, zinc and lead oxides, which possess approximately the same heat conductivity, should accelerate vulcanization to approximately the same degree. A compound containing aluminum bronze should vulcanize faster than either of the above, but Seidl demonstrated that such is not the case, for a compound containing litharge vulcanized in less time than a similar compound containing aluminum bronze. This theory is therefore thoroughly discredited.

A theory proposed later assumed that by formation of lead sulfide, in a vulcanizate resulting from reaction of the litharge with sulfur, the molecule S_8 is split, releasing a portion of the sulfur in a nascent state, causing an intensive sulfurizing of the rubber. We shall see later that this theory, which was soon abandoned, was reasonably close to the present conception of the phenomenon. It was established by numerous investigators that lead sulfide itself caused no acceleration and that the litharge undergoes no combination with the rubber. Furthermore, Seidl showed that the resins in the rubber react with sulfur, forming hydrogen sulfide, and that litharge promotes the reaction. In arriving at these conclusions, Seidl prepared compounds containing (1) Para rubber, (2) acetone-extracted (resin-free) Para rubber, (3) Para rubber prepared as in (2) but further purified by solution in petroleum ether and precipitation with alcohol. All compounds contained litharge and sulfur. The bulb of a thermometer was coated with these compounds and heated to 140° C. At this point the temperature on the inside of the compound was higher than the temperature of the heating medium. The rise in temperature was greatest in compound (1), somewhat less in compound (2), and very slight in compound (3). Seidl believed, therefore, that a thermal reaction would explain the accelerating effect of litharge. The accelerating action of the litharge is due to a higher temperature during

[95] *Gummi-Ztg.*, **30**, 303, 326 (1916). [96] *Gummi-Ztg.*, **25**, 710, 748 (1911).

vulcanization in a compound containing litharge than in compounds containing other inorganic materials. According to Seidl, the rise in temperature was caused by reaction between litharge and hydrogen sulfide,[97] the latter resulting from interaction of sulfur and resins (or other non-rubber constituents) with evolution of heat. This reaction proceeds with sufficient velocity only if the hydrogen sulfide is chemically combined immediately. If the resins are removed from the rubber, only a slight rise in temperature occurs, and accordingly only a slight acceleration is produced. If the rubber is separated from all its natural impurities, the litharge exerts no accelerating action, and only traces of lead sulfide are formed during vulcanization. Traces of lead sulfide owe their presence to the reaction [98]

$$4\,PbO + 4S = PbSO_4 + 3PbS$$

Finally, Seidl succeeded in partially restoring the accelerating action of litharge with reprecipitated rubber, by the addition of an oily distillate obtained by the destructive distillation of blood albumin. Since the albumin product reacted less readily with sulfur than the non-rubber constituents of the rubber, the accelerating action produced by the litharge was less in this experiment than in that with whole rubber.

As interesting as these experiments and the conclusions drawn by Seidl may be, they are hardly in accord with the facts. Otherwise, for example, all large rubber articles vulcanized in metal forms would necessarily show a higher vulcanization coefficient at the center than at the surface, where the heat would be conducted away. Seidl's views did not remain unchallenged as they were attacked especially by Esch and Auerbach.[99] The importance of the rubber resins for the accelerating action of litharge as established by Seidl, was, however, fully and completely confirmed later by L. E. Weber and H. P. Stevens. Weber's [100] experiments showed that resin-free rubber when compounded with litharge, whiting, and sulfur, vulcanized poorly. Stevens [101] found that vulcanization, as indicated by vulcanization coefficients, proceeded more slowly in the case of acetone-extracted rubber in the presence of litharge than did vulcanization of natural rubber with litharge under similar conditions. When further additions of rubber resins were made to the compound containing unextracted rubber, the vulcanization coefficient could be raised still further under the same experimental conditions. G. D. Kratz and A. H. Flower [102] have demonstrated that the natural non-rubber constituents of rubber have the same importance in mixtures containing magnesium oxide. Stevens [103] conducted similar experiments dealing with the action of litharge and magnesia, by adding increasing amounts of each to mixtures containing 90 parts of light plantation crepe rubber and 10 parts of sulfur. He vulcan-

TABLE 10.—*Effect of Magnesia and Litharge on Vulcanization.*

Magnesia	Vulcanization Coefficient	Litharge	Vulcanization Coefficient
.....	1.40	.....	1.26
0.10	2.66	0.10	1.25
0.25	3.31	0.25	1.27
0.40	3.68	0.50	1.37
0.75	4.08	0.80	1.75

[97] $PbO + H_2S = PbS + H_2O + 73.9$ Calories.
[98] According to Seidl's experiments, the reaction does not proceed as in the equation: $2PbO + 2S = 2PbS + O_2$.
[99] *Gummimarkt*, **5**, 123 (1911).
[100] *Orig. Comm. Eighth International Congress of Applied Chem.*, **9**, 95 (1912).
[101] *Ibid.*, **9**, 581 (1912); *J. Soc. Chem. Ind.*, **35**, 874 (1916); **37**, 156 (1918).
[102] *Chem. and Met. Eng.*, **20**, 417 (1919); *Ind. Eng. Chem.*, **12**, 971 (1920).
[103] *Orig. Comm. Eighth International Congress of Applied Chem.*, **9**, 581 (1912).

ized the resulting compounds for one hour at 138° C., and determined the vulcanization coefficients. As may be seen in Table 10, magnesia in small amounts is a more powerful accelerator than litharge. However, the curves obtained from physical tests on the vulcanizates showed that at higher accelerator concentrations, litharge reached the same activity as magnesia.

J. M. Grove[104] has carried out comparative experiments, using litharge, basic lead carbonate (white lead), pure basic lead sulfate, and basic lead sulfate contaminated with lead sulfide. He determined the amount of each necessary to attain the same acceleration of vulcanization. A mixture containing 80 parts of rubber, 2½ parts of sulfur and 5 parts of zinc oxide was made up to 100 parts with these lead compounds and heavy spar (barytes). Setting the amount of litharge at 1, the equivalent amounts of pure basic lead sulfate and of basic lead carbonate were about 3, while with the lead sulfide-contaminated sample of basic lead sulfate, 7 parts were required. It might also be mentioned that P. Breuil[105] has shown that lead oxychloride shows an accelerating action, although the compound has as yet found as little use as basic lead sulfate.

In addition to magnesia, basic magnesium carbonate is much used in compounding rubber.[106] Opinions still vary concerning the action of this compound. For example, P. Breuil[107] and B. D. Porrit[108] claim that it acts as an accelerator, while K. Gottlob[109] considers it to be only a pigment.

As already mentioned at the beginning of this section, the powerful accelerating action of lime (calcium hydroxide) is well known. On the other hand, zinc oxide possesses only slight accelerating action, as established by Beadle and Stevens[110] (*see* p. 332). Other inorganic accelerators mentioned in the literature are ferric oxide,[111] arsenic trisulfide,[112] antimony pentasulfide (Goldschwefel),[113] polysulfides such as zinc polysulfide,[114] and sodium hydroxide. With respect to the latter compound, W. G. Martin[115] points out that small amounts decrease the time of vulcanization of rubber compounds considerably, while larger amounts (over 0.5 per cent) possess the opposite function, that is, they retard vulcanization. With an addition of 5 per cent, the compound chosen by Martin for experimental purposes would no longer vulcanize correctly. This compound contained 38¼ per cent of Para rubber, 60 per cent of zinc oxide, and 1¾ per cent of sulfur.* Martin called attention to the importance of these observations in connection with compounds containing alkali reclaim, from which the alkali has not been completely washed out (*see* p. 344).† In conclusion, it may be mentioned that E. Seidl[116] found sodium peroxide to act as an accelerator and that in 1881, T. Rowley[117] used ammonia for the vulcanization of rubber. The use

[104] *India Rubber World*, **64**, 663 (1921).
[105] *Caoutchouc and gutta-percha*, **4**, 1415 (1907).
[106] The composition of this compound is ordinarily assumed to be $4\ MgCO_3 \cdot 3\ Mg(OH)_2 \cdot 5\ H_2O$. According to H. W. Greider [*Ind. Eng. Chem.*, **14**, 385 (1922)] it corresponds more nearly to the formula $11\ MgCO_3 \cdot 3\ Mg(OH)_2 \cdot 11\ H_2O$.
[107] *Caoutchouc and gutta-percha*, **4**, 1352 (1907).
[108] "The Chemistry of Rubber," p. 42, Gurney & Jackson, London, **1913.**
[109] "Technologie der Kautschukwaren," p. 70, Braunschweig, **1915.** *See* also A. van Rossem, Dissertation, p. 192, Amsterdam, **1916.**
[110] *J. Soc. Chem. Ind.*, **30**, 1421 (1911).
[111] Ditmar, *Gummi-Ztg.*, **29**, 424 (1914).
[112] Twiss, *India Rubber J.*, **65**, 696 (1923).
[113] King, *Chem. & Met. Eng.*, **15**, 231 (1916); Anderson and Ames, *J. Soc. Chem. Ind.*, **42**, 136 (1923).
[114] Bedford and Sebrell, *Ind. Eng. Chem.*, **14**, 25 (1922).
[115] "The India Rubber Industry," p. 205, London, **1914**; *Cf.* also, W. Esch: Ger. Pat., 344,061 (1919).
* Translator's Note. Five per cent of sodium hydroxide in this compound is more than the chemical equivalent of the sulfur present. It is conceivable that the compound should not have vulcanized at all.
† Translator's Note. *See* Palmer and Kilbourne and Miller, *Ind. Eng. Chem. Anal. Ed.*, **3**, 45 (1930).
[116] *Gummi-Ztg.*, **25**, 748 (1911).
[117] Brit. Pat., 787 (1881).

of ammonia is not without interest in relation to later work on organic vulcanization accelerators.

More recently, C. W. Bedford and H. A. Winkelmann [118] have studied the mechanism of acceleration of vulcanization by inorganic compounds and have confirmed Seidl's [119] observation that the phenomenon is absent if the rubber has been deresinated by acetone extraction. Furthermore, they showed that the accelerating action is increased by addition of organic acids such as oleic and stearic acids. They concluded, therefore, that the mutual action of the inorganic basic compounds and the acid non-rubber constituents, the so-called resins, was necessary for acceleration. Furthermore, they assumed that mixed salts are formed, which under the action of elementary sulfur form polysulfides. These readily split off "active" sulfur, i. e., sulfur in the atomic condition.

$$2\text{R-COO-Pb-SH} + \text{S} \longrightarrow \text{R-COO-Pb-S-S-Pb-OOC-R} + \text{H}_2\text{S}$$

According to this theory, metallic salts which are soluble in the rubber must first be formed in order that polysulfides, the real accelerators, may be produced. This explanation appears to be all the more plausible because of the fact that ammonium, potassium, and sodium polysulfides bring about vulcanization even in the absence of elementary sulfur and therefore must contain sulfur in an especially active form. In this connection, it may be mentioned that F. Dannerth [120] has reported the accelerating action of metallic oleates and stearates.

Although Bedford and Winkelmann could not prove the presence of such lead soaps in litharge-containing compounds, by extraction (for example, with benzene and alcohol) and identification, they showed instead, that the same action is produced, when the lead soaps as such, or the individual constituents necessary for their formation, are present in the rubber mixture. It was furthermore established that these lead soaps are soluble in rubber, and that lead soaps which are soluble in benzene act as vulcanization accelerators in resin-free rubber mixtures, while this is not the case with those insoluble in benzene. The solubility of the metallic compounds formed during vulcanization appears to be the determining factor with regard to accelerating action. The fact that zinc oxide, for example, exerts no accelerator action in a rubber-sulfur mixture despite its basicity, must be explained by the insolubility of the zinc soaps in rubber, or the non-reaction of zinc oxide with the acids (*see* p. 332). As we shall see later (*see* p. 324), the addition of other organic substances which produce soluble zinc compounds in rubber, results in the production of an especially powerful accelerator from the zinc oxide.

Although the theory of Bedford and Winkelmann explains so many of the known facts, it, nevertheless, offers no logical reason why litharge should exert such different accelerating actions on various kinds of rubber. C. O. Weber [121] had already observed that Mangabeira and certain African varieties of rubber in mixtures containing small amounts of sulfur did not vulcanize even in the presence of litharge. These data refer to vulcanization in hot air. It is a known fact that the three methods of vulcanization (in hot air, in steam or hot water, and between heated plates of a press), can produce different results on the same compound at the same temperature. Results ob-

[118] *Ind. Eng. Chem.*, **16**, 32 (1924).
[119] *Gummi-Ztg.*, **25**, 710, 748 (1911).
[120] *India Rubber World*, **64**, 563 (1921); *Cf.* also H. Feuchter, *Kolloidchem. Beihefte*, **19**, 47 (1924).
[121] *Gummi-Ztg.*, **16**, 931 (1902); **17**, 898 (1903); **19**, 83 (1904).

tained by the use of any one method are not properly to be compared with those using the other methods. However, we shall see that in this case this difference in procedure is not of principal importance for the action of litharge.

Acting on Weber's results, B. Bysow [122] conducted experiments at a later date on hot air vulcanization in the presence of litharge. He demonstrated that here also the resins play an important part, by showing that acetone-extracted Para rubber would not vulcanize in hot air. Without extraction of the resins, Para, plantation crepe, Ceara, Guayule, and Accra lump, vulcanized well, while Upper Congo, Benguella, Kassai and Peruvian rubbers failed to vulcanize under the same conditions. Consequently, other circumstances besides the presence of resins must enter into the question, especially since the non-vulcanizing varieties become capable of vulcanization upon addition of a resin of an acid character, such as colophony or shellac. The next thing, then, was to determine the acidity of the resins. The acid numbers in Table 11 were obtained by Bysow on titration with alcoholic potassium hydroxide.

TABLE 11.—*Acidity of Rubber Resins.*

Kind of Resin	(a) Resin content of the rubber	(b) Acid number of the resin	(a x b) Acidity in mg. of KOH based on 100 grams of rubber
Para	3	98	294
Plantation crepe	3-2	45-93	135-186
Ceara	4	43	172
Guayule	20	12	240
Accra lumps	26	2.9	75.5
Upper Congo	3-4	12	43
Benguella	6	10	60
Kassai	4	8	32
Peruvian	3	6	18

There are seen here wide differences in acidity of the various kinds of wild rubber, just as Whitby and Winn (*see* p. 308) showed in the various kinds of plantation rubber. Furthermore, it appears that for hot-air vulcanization in the presence of litharge, there is required a minimum total acidity, equivalent to 60 to 75 mg. of potassium hydroxide, since Accra lumps can be vulcanized, while Benguella rubber cannot. Bysow further established this limiting value by showing that a mixture consisting of 100 parts Benguella, 30 parts litharge and 3 parts sulfur (the mixture alone could not be vulcanized) could be vulcanized satisfactorily if as little as 0.3 part of stearic acid were added. The stearic acid could be replaced also by palmitic, oleic, or cinnamic acids, while citric and salicylic acids were inactive. This leads to the deduction that the melting point of the acid, as well as the solubility of its lead salt in rubber, is important. Investigations leading to the determination of the minimum amount of litharge required for satisfactory vulcanization were carried out by Bysow on the above-described compound with Benguella rubber and the added stearic acid. Approximately 4 parts of litharge was the minimum quantity which would produce a good vulcanizate. In addition to the acids named, the following substances are also active in promoting vulcanization: beeswax, Japan wax, carnauba wax and spermaceti, as well as raw sugar and certain polyvalent phenols. However, phenol, guaiacol, alpha-naphthol, and resorcinol, were inactive. The lead salts favoring hot vulcanization were basic lead carbonate and acetate, as well as lead palmitate, oleate, and stearate, while the neutral salts such as lead carbonate, sulphate,

[122] *India Rubber J.*, **71**, 99 (1926).

oxalate, chromate, nitrate, sulfite, and calcium plumbate were inactive. Bysow considered mercury and silver oxides analogous to litharge. As pointed out above, all of Bysow's work refers only to the special case of hot-air vulcanization, though in spite of this, his work unquestionably led to the same conclusions reached by Bedford and Winkelmann. That is to say, if lead salts which are not of themselves active are added to a rubber mixture, the accelerating action of the inorganic compounds is determined largely by the rubber resins, since reaction with these non-rubber constituents produces compounds soluble in rubber. Furthermore, not only the amount but the acidity of the resins is a determining factor with regard to accelerating action.

Bedford and Winkelmann had pointed out that the vulcanizing action of litharge in a rubber-sulfur mixture is increased by addition of the higher fatty acids, but other investigators included also the lower acids of this series in their investigations. Thus C. Dekker [123] had determined that the acetone-soluble constituents of first latex sheet contained water-soluble acids, in addition to the various liquid and solid fatty acids and their esters. A. van Rossem and P. Dekker [124] vulcanized mixtures which contained, in addition to 92.5 parts of acetone-extracted rubber, 7.5 parts of sulfur and 10 parts of litharge, also 1.5 per cent of stearic acid (based on the rubber) or the equivalent molecular quantities of the lower fatty acids. The period of heating was 10 minutes at 147° C. In the presence of litharge the same action was exerted by stearic, lauric, caproic, butyric, propionic, and acetic acids, but formic acid failed to act. The action of these acids is best shown by the results of the experiments, which these investigators conducted by making 5 per cent cements of the mixtures in benzol, and heating them at 147° C. in pressure flasks with the calculated amounts of fatty acids. The data in Table 12 were obtained in this way.

TABLE 12.—*Action of Fatty Acids on Vulcanization.*

Material	Results
Mixture containing no acid	No gelation after 120 minutes
Mixture containing stearic acid	Gelation after 10 minutes
Mixture containing propionic acid	Gelation after 10 minutes
Mixture containing acetic acid	Gelation after 10 minutes
Mixture containing formic acid	No gelation after 120 minutes

According to van Rossem and Dekker, the part played in accelerating vulcanization in the presence of litharge by the fatty-acid esters present in the acetone extract, depends on the ability of the oxide to split the esters and form lead soaps.

P. H. Mitchell [125] has carried out similar investigations with mixtures, in which he used zinc oxide. Acetone- and water-extracted smoked sheets were used, and quantities of various fatty acids equivalent to the total acidity of the acetone extract of the rubber were added. In addition to sulfur, each mixture contained zinc oxide equivalent to the added acid. The optimum time of vulcanization was determined for all mixings. The author concluded that the chief action of the fatty acids consisted in dispersing the zinc oxide and other compounds, thereby increasing the accelerating action. W. H. Smith and C. E. Boone [126] have studied the same problem with compounds which contained 100 parts of brown crepe, 10 parts of sulfur, 5 parts of zinc oxide, and 1/15 mol of saturated fatty acid (from the series comprising formic to nondecylic acid

[123] *India Rubber J.*, **70**, 815 (1925).

[124] *Ind. Eng. Chem.*, **18**, 1153 (1926).

[125] *Caoutchouc and gutta-percha*, **23**, 13,340 (1926); **24**, 13,440 (1927).

[126] *Ind. Eng. Chem.*, **19**, 398 (1927).

($C_{19}H_{38}O_2$), per 1000 g. of rubber. The period of heating was 50 minutes at 149° C., and the tensile strength was determined. When the tensile strengths were determined it developed that the tensile values for the compounds containing acids with an uneven number of carbon atoms lay on a different curve from that obtained for the compounds containing acids with an even number of carbon atoms. In the series of acids containing from one to nine carbon atoms, those with an uneven number of carbon atoms produced the higher tensiles, while in the series of acids containing from eleven to nineteen carbon atoms, the members with an odd number of carbon atoms gave lower values. Thus a periodic variation exists, as is already known in regard to melting points and heats of crystallization. In an investigation with light crepe, a similar but much less striking variation was found.

From the foregoing discussion, it may be seen that the observations of Bedford and Winkelmann, and with these the work of other authors as well, have considerably advanced our knowledge of inorganic accelerators. It is certain that the acidity of certain acetone-soluble constituents of crude rubber is of great importance, and it is very probable that the activity of the soaps formed depends on their solubility in rubber. As to how these soaps act as sulfur activators, there is no generally accepted theory. It is not considered entirely impossible that some factors other than sulfur activation are of importance.

Organic Accelerators

The theory of Bedford and Winkelmann that the inorganic accelerators are not such of themselves until after reaction with organic acids, leads directly to a more recent group of accelerators which has become of the greatest importance in rubber goods manufacture.

The work of chemists of the Elberfelder Farbenfabriken vorm. Bayer & Co.[127] on the vulcanization of synthetic rubber was the occasion of the discovery of these so-called organic accelerators.* K. Gottlob,[128] who was one of these chemists, writes as follows concerning the discovery of such compounds:

"There are certain kinds of synthetic rubber which decompose quickly in air through oxidation. These kinds of rubber can, however, as the Farbenfabriken vorm. Bayer & Co. has found, be protected against oxidation very effectively if a small quantity of organic base is mixed with them. As protectives, such bases as aniline, pyridine, quinoline, dimethylamine, and in certain cases piperidine were used. While the bases mentioned first in the above list produced no essential change during the vulcanization of the particular variety of rubber involved, the rubber in which 1 per cent of piperidine was used showed a completely different behavior after vulcanization, which was ascribed to a very far advanced vulcanization. The determination of combined sulfur showed that about eight times as much sulfur had combined with the rubber, as the expected amount under normal conditions, a truly astonishing result. This observation, which was made jointly by F. Hofmann, the chief of the rubber

[127] According to W. C. Geer [*Ind. Eng. Chem.*, **14**, 372 (1922)] Marks and Oenslager used organic substances such as aniline in 1906, and thiocarbanilide in 1907. D. Spence [*J. Soc. Chem. Ind.*, **36**, 118 (1917); *J. Ind. Eng. Chem.*, **10**, 115 (1918)] had used organic compounds such as piperidine prior to 1912. The first publication, however, on this subject was the Ger. Pat., 265,221 by the Elberfelder Farbwerke in the year 1912.

* Translator's Note. See the Perkin Medal Address, "Organic Accelerators," by George Oenslager, *Ind. Eng. Chem.*, **25**, 232 (1933).

[128] *Gummi-Ztg.*, **30**, 303, 326 (1926).

division of the Farbenfabriken vorm. Bayer & Co., and K. Gottlob, induced us to investigate the action of piperidine on the vulcanization of natural rubber, whereby entirely similar results were obtained. This action was possessed not only by piperidine and its homologues but, as was found later, by certain solid addition products of the bases which at the vulcanization temperature obviously dissociated and became active. This was very gratifying, since piperidine itself is very volatile and partially escaped from the rubber on the hot rolls. Furthermore, certain aliphatic bases, dimethylamine, tetramethylenediamine, and derivatives of these bases, showed the same accelerating action, on further investigation.[129] Finally, in conjunction with Bögemann, I succeeded in demonstrating that not only the above-named bases, but all bases, including the aromatic, possess an accelerating action, provided their dissociation constant is above a certain limit. This limit, above which lie the dissociation constants of those bases which are practically effective, is approximately 10^{-8}. That it is the basicity only, rather than the chemical constitution of the substance, which primarily governs its effectiveness, is shown very beautifully by an experiment with para-, ortho-, and meta-phenylenediamine. The first of these, being a very strong base, accelerates vulcanization very powerfully, while the other two, whose dissociation constants lie below 10^{-8}, are almost without action. Bases having dissociation constants greater than 10^{-5} accelerated enormously, 'Vulkacit A Bayer' (*see* p. 368), in fact, accelerating vulcanization approximately ten times as much as the known inorganic accelerators."

It is also important historically, as established by K. Gottlob, "that the absolute value of the tensile strength is somewhat higher with (12 kg.) than without (10.5 kg.) accelerator. Since this phenomenon is checked by other experiments, I am of the opinion that the speed with which the desired degree of vulcanization is reached influences the mechanical properties favorably, the nerve of the rubber, which always suffers under long heating, being thereby protected." The correctness of Gottlob's views was to be recognized later.

The Elberfelder Farbenfabriken, as we have just seen, ascribed the accelerating action to the basicity of the organic substances. G. D. Kratz, A. H. Flower and B. J. Shapiro [130] later established that phenylhydrazine, which has a dissociation constant of 1.6×10^{-9}, does not accelerate vulcanization. On the contrary, its presence retards vulcanization. From this and other experiments,* these investigators concluded that the accelerating activity of organic bases is not proportional to their basicity. The discovery of the accelerating action of nitroso compounds by S. J. Peachey [131] was another blow to the basicity theory. Peachey first recognized that para-nitrosodimethylaniline and its homologs, later para-nitrosophenol and para-nitrosocresol,[132] and finally nitrosobenzene [133] act as accelerators, while para-aminophenol is without effect on the rate of vulcanization. Since it could no longer be held that the basicity of an organic base was the only controlling factor in its accelerating action, and

[129] Ger. Pat., 269,512 (1913); 280,198 (1914).
[130] *Ind. Eng. Chem.*, **13**, 67 (1921).
[131] Ger. Pat., 323,088 (1920); Brit. Pat., 4,253 (1914).
[132] Ger. Pat., 328,611 (1920); Brit. Pat., 101,819 (1916).
[133] Brit. Pat., 136,716 (1919).

* Translator's Note. Among these other experiments, was one in which it was shown that meta-phenylenediamine with a low dissociation constant (1.35×10^{-12}), was a better accelerator than certain other bases with higher dissociation constants, e. g., phenylhydrazine.

since all the known accelerators contained nitrogen, it was claimed that this element was responsible for the accelerating action. The discovery of nitrogen-free accelerators such as the zinc alkyl xanthates by J. Ostromislensky,[134] and zinc thiophenol by C. W. Bedford and L. B Sebrell,[135] caused the rejection of all of the old theories.

The first publications of the Elberfelder Farbenfabriken naturally aroused the interest of the technical world. A glance at the literature of the last fifteen years reveals the intense activity in this field. It would be impossible to note all the publications here or to list, even partially, all the compounds possessing accelerating action. The most essential developments only can be considered.

Several hundred compounds having accelerating action are already known. They may be grouped, according to Luff-Schmelkes,[136] in the following divisions:*

Nitrogen-containing accelerators. Ammonia derivatives of aldehydes: Hexamethylenetetramine ("HMT," "Hexamin" or "Hexa"), aldehyde-ammonia, furfuramide ("Vulkazol"), hydrobenzamide.

Aliphatic amines and piperidine, as well as their sulfur addition products, such as piperidinium pentamethylenedithiocarbamate and dimethylammonium dimethyldithiocarbamate, as well as the reaction products of these with aldehydes, such as benzaldehyde-diethylimide.

Aromatic amines, such as aniline, methylaniline, dimethylaniline, toluidine, phenylenediamine, dimethyl-para-phenylenediamine and diphenylamine, as well as their compounds with aldehydes, such as formaldehyde-phenylimide, dianilinomethane, benzaldehyde-phenylimide, and their compounds with carbon disulfide, such as symmetrical diphenylthiourea and di-ortho-tolylthiourea.

Guanidines such as mono-, di- and symmetrical triphenylguanidine.

Nitroso compounds, such as para-nitrosodimethylaniline (Accelerene), para-nitrosodiphenylamine, nitrosobenzene and para-nitrosophenol.

Thiuramdisulfides, which are formed by treating dithiocarbamates with mild oxidizing agents or halogens:

$$2\ R_2N-CS-SHNHR_2 \xrightarrow{Br_2} R_2NC(=S)-S-S-C(=S)NR_2 + 2R_2NH\cdot HBr$$

for example, tetramethyl- or dipentamethylene-thiuramdisulfide.

Miscellaneous compounds. Certain dye bases (triphenylmethane dye bases),[137] benzene sulfamide, phenylhydroxylamine and the reaction product of aldehyde-ammonia with carbon disulfide (carbothialdin).

[134] *J. Russ. Phys. Chem. Soc.*, **47**, 1441 (1915); *Gummi-Ztg.*, **30**, 991 (1916).

[135] *Ind. Eng. Chem.*, **13**, 1034 (1921).

[136] "Die Chemie des Kautschuks," p. 155, Berlin, **1925**.

* Translator's Note. A number of articles dealing with the classification and uses of accelerators have appeared in recent years. A few of the more important classifications are here given, in the hope that they may be of value for reference use.

R. P. Dinsmore and W. W. Vogt, *Rubber Age (N. Y.)*, **23**, 554-557 (1928); *Rubber Chem. Tech.*, **1**, 410 (1928).

W. Norris, *India Rubber World*, **79**, No. 3, 53-57 (1929); **79**, No. 4, 66 (1929).

F. Emden, *Kautschuk*, **5**, 241-244, 269-276 (1929); *Rubber Age (N. Y.)*, **26**, 599-603, 659-661 (1930).

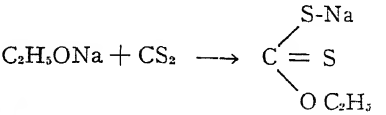
G. Martin and R. Thiollet, *Caoutchouc and gutta-percha*, **26**, 14,494-14,497; 14,722-14,730 (1929); *Rubber Chem. Tech.*, **2**, 350-361 (1929); **3**, 38 (1930); *Rubber Age (N. Y.)*, **25**, No. 4, 201 (1929).

F. Jacobs, *Caoutchouc and gutta-percha*, **27**, 15,165-15,172, 15,258, [illegible]; **28**, 15,350, 15,394, 15,438, [illegible]; 15,562, 15,602, 15,638, 15,674, [illegible] (1931); **29**, 15,836, 15,870, [illegible]; 15,978, 16,014, 16,050, 16,082, [illegible]; 16,186 (1932); **30**, 16,258, [illegible]; 16,389, 16,421, 16,509, 16,541, [illegible].

P. Bary, *Rev. gén. caoutchouc*, **6**, No. 53, 3 (1929); **7**, No. 59, 3 (1930).

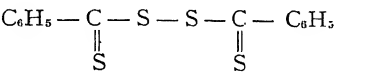
[137] L. Gaisman and J. L. Rosebaum, Brit. Pat., 141,412 (1919).

Nitrogen-free accelerators. Xanthates, i. e., the reaction products of carbon disulfide with alcoholic alkali solutions.



in the form of their sodium, potassium, zinc, and lead salts in the presence of zinc oxide.

Salts of dithioacids [138] such as zinc dithiobenzoate, and the corresponding disulfides [139] such as dithiobenzoyl disulfide.



Anthraquinone and benzoquinone, which S. J. Peachey [140] used for the cold vulcanization of rubber with hydrogen sulfide and sulfur dioxide.

As we shall see later, the number of types of compounds with accelerating action is not exhausted with the above list.

It was stated previously that these organic accelerators are of great importance to the rubber industry and it might therefore be well to discuss the advantages which they offer over the longer known inorganic accelerators.

Early publications show that organic accelerators were used mainly to shorten the time of vulcanization, or as K. Gottlob [141] stated, "to economize on time, steam, equipment, molds, and labor." It was also quickly realized that, whereas large amounts of inorganic compounds were required to accomplish the desired acceleration, as little as 1 per cent of organic accelerator, based on the rubber content of the compound, was required. The advantage for certain purposes is that the specific gravity of the compound is practically unchanged by the use of the accelerator. Gottlob further points out that by the use of organic accelerators a lower sulfur content may be used in the compound than when inorganic accelerators are used, thus diminishing the danger of after-curing and undesirable blooming of free sulfur. Gottlob also suggested that decreasing the time in which a desired state of vulcanization is attained influences the mechanical properties of the vulcanizate favorably. As we shall see later, the chief value of organic accelerators is to be attributed to this latter property directly, for with the help of these substances and recent knowledge of the pigmentation of rubber, the mechanical properties of rubber goods have been raised to heights never attainable in former times with inorganic accelerators. It was soon learned that some compounds not only decreased the time of vulcanization but also lowered the temperature necessary for vulcanization, indeed making vulcanization even at room temperature possible. It is of special interest that the optimum mechanical properties are reached at a vulcanization coefficient much lower than was earlier the case with inorganic accelerators or without any accelerator. This lower content of combined sulfur is noticeably reflected in the better aging properties of the vulcanizate. The term accelerator is really not comprehensive enough, since the substances

[138] G. Bruni, *India Rubber J.*, **64**, 937 (1922); **65**, 238 (1923).
[139] E. Romani, *Caoutchouc and gutta-percha*, **19**, 11,626 (1922); **20**, 11,679, 11,720 (1923).
[140] Brit. Pat., 190,051 (1922).
[141] *Gummi-Ztg.*, **30**, 326 (1916).

thus designated serve as vulcanizate improvers, in addition to their action in reducing the vulcanization time.[142]

Theories of Accelerator Action

It is easy to understand that the multiplicity of interesting phenomena arising from the results of vulcanization in the presence of organic accelerators has directed the interest of many chemists toward the mechanism of the reaction between these substances and rubber. It was soon recognized that the action of accelerators is not truly catalytic. The large variety of accelerator types led investigators to surmise that no single formula would explain the action of all. It is generally accepted, especially with reference to the decrease in time and temperature of vulcanization, that elementary sulfur is rapidly changed under the influence of accelerators into a more active form, thus promoting its combination with the rubber hydrocarbon. The discovery of the Peachey process of vulcanization (*see* p. 334), by which nascent sulfur is produced in the rubber, making possible an almost instantaneous vulcanization at room temperature, supports this theory. On the other hand, M. Le Blanc and M. Kröger[143] have shown that the viscosity of rubber sols decreases with increasing dielectric constant of the solvent and suffers a further reduction on addition of an accelerator. It might be assumed from this observation that in some way the accelerator acts directly upon the rubber hydrocarbon. It is generally assumed today that the elementary sulfur which is mixed with the rubber combines with the accelerator to produce compounds which can easily split off sulfur. This nascent sulfur is then the active vulcanizing agent. The fact that the accelerators belong to such widespread classes would indicate that their chemical action should likewise differ widely. For this reason, a generally applicable theory for accelerator action has not yet been advanced.

The first to attempt to develop such a theory was Ostromislensky.[144] Basing his theory on the observations of H. Erdmann,[145] concerning the vulcanization process, he assumed that primary and secondary amines, especially in the presence of metallic oxides, form thio-ozonides.

$$2RNH_2 + 4S \longrightarrow RNHS-S-SNHR + H_2S$$

These then yield sulfur in an active form by reversion of the reaction or with formation of compounds of the type RNH · NHR. Even if elimination of all the sulfur from a thio-ozonide is hardly possible (for it would probably act as does an ozonide), there is furthermore, opposed to this conception, the fact that at a later date, trimethylamine,[146] which has no hydrogen combined with the nitrogen, became known as a powerful accelerator.

G. D. Kratz, A. H. Flower and C. Coolidge[147] explain the accelerating action of compounds containing nitrogen, especially of the amines, by assuming that the nitrogen atoms add sulfur by a change in valence from three to five. By a reversion of the process, these addition compounds should yield sulfur in an active form.

$$RNH_2 + S \longrightarrow RNH_2S \longrightarrow RNH_2 + S \text{ (active)}$$

These assumptions are supported by the fact that para-phenylenediamine,

[142] F. Hofmann, *Chem.-Ztg.*, **50**, 1006 (1926).
[143] *Z. Elektrochem.*, **27**, 335 (1921).
[144] *J. Russ. Phys. Chem. Soc.*, **47**, 1892, 1898 (1915); *J. Soc. Chem. Ind.*, **35**, 370 (1916); *Caoutchouc and gutta-percha*, **13**, 8946, 9034, 9064, 9362 (1916).
[145] *Ann.*, **362**, 133 (1908).
[146] A. Dubosc, *Caoutchouc and gutta-percha*, 10,050 (1919).
[147] *J. Ind. Eng. Chem.*, **12**, 317 (1920).

with two reactive amine groups, was found to be approximately twice as active as aniline, with only one.

A. Dubosc [148] attributes the activation of sulfur by metallic oxides to the joint action of hydrogen sulfide and sulfur dioxide, the former resulting from reaction of sulfur with the resins and proteins of the rubber, and the latter being produced by reaction of sulfur with metallic oxides. Aside from the fact that this conception is limited to metallic oxides, the author does not consider the question as to whether sufficient amounts of the gases are formed in the requisite proportions to satisfy the following equation:

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S$$

In addition, Dubosc assumes that the organic accelerators containing nitrogen react with sulfur to form thiocyanic acid, which serves as an activating agent, by giving up its sulfur to the rubber hydrocarbon. In the course of these reactions hydrocyanic acid, which in turn is capable of adding sulfur again, is formed. The mechanism which Dubosc devises for the formation of thiocyanic acid by reaction of sulfur with aniline, is quite doubtful. It might also be inquired whether under the existing conditions, thiocyanic acid might not simply be added (analogously to the addition of free thiocyanogen) [149] to the double bond. It might be mentioned here, however, that L. B. Sebrell [150] was able to detect thiocyanic acid among the reaction products of hexamethylenetetramine and sulfur. It is also interesting that Dubosc conceives the thiocyanic acid as a condensing agent for the rubber hydrocarbon. Thus there is presented for the first time the idea that a variety of actions take place during vulcanization, leading on the one hand to increasing the degree of vulcanization and on the other to the improvement of the mechanical properties through the presence of the accelerator.

Although the previously discussed theories applied essentially to the nitrogen-containing accelerators (for example the amines), by means of the theories of C. W. Bedford and W. Scott [151] it was possible to interpret the known facts for a larger number of types of accelerators. They assume that the intermediate formation of polysulfides, as a source of active sulfur, takes place. For amines, for example, the following reaction would occur:

$$\text{R-NH}_2 + \text{H}_2\text{S} \longrightarrow \text{R-}\overset{\text{H}}{\underset{\text{SH}}{\text{N}}}\text{H}_2 + x\text{S} \longrightarrow \text{R-}\overset{\text{H}}{\underset{\text{S}x=\text{SH}}{\text{N}}}\text{H}_2 \longrightarrow \text{R-}\overset{\text{H}}{\underset{\text{SH}}{\text{N}}}\text{H}_2 + x\text{S (active)}$$

Thus the polysulfide is assumed to split off active sulfur. The hydrogen sulfide necessary for reaction with the accelerator results from the reaction of sulfur with the natural non-rubber constituents of the rubber. In favor of this hypothesis is the fact that amines, for example dimethylamine, absorb hydrogen sulfide rapidly, yielding a red polysulfide solution. The observation of D. F. Twiss [152] that the acceleration of vulcanization in the presence of potassium hydroxide is uninfluenced when its solution in glycerol is saturated with hydrogen sulfide to convert it to potassium hydrosulfide, bears out the theory. The accelerating action of the hydroxide appears not to be due to the hydroxyl group, but to the capacity for hydrosulfide

[148] *Caoutchouc and gutta-percha*, **14**, 9109 (1917); **17**, 10,511 (1920).

[149] Pummerer and Stärk, *Ber.*, **64**, 829 (1931); *Rubber Chem. Tech.*, **4**, 402 (1931).

[150] Bedford and Winkelmann, "Systematic Survey of Rubber Chemistry," p. 32, Chemical Catalog Co., Inc., New York, **1923**.

[151] *Ind. Eng. Chem.*, **12**, 31 (1920); **13**, 125 (1921); *see* also Bedford and Sebrell, *ibid.*, **13**, 1034 (1921); **14**, 25 (1922).

[152] *J. Soc. Chem. Ind.*, **36**, 782, 1185 (1917); **40**, 242 (1921).

formation, followed later by polysulfide formation. If one considers the following facts: (1) the experiments of Bedford and Sebrell in which they prepared (by reaction of sulfur dioxide and hydrogen sulfide in benzene below 10° C.) the very active accelerator, trithio-ozone, which they consider to be a polysulfide of sulfur and which produces vulcanization at room temperature; (2) that Ph. Schidrowitz in his "Vultex" process vulcanizes latex by using polysulfides (*see* p. 90); and (3) that an explanation is offered by the polysulfide theory for the effectiveness of small amounts of accelerator in activating proportionately large amounts of sulfur; then it may be seen that the polysulfide theory has much in its favor. The accelerators which are capable of forming polysulfides were designated by Scott and Bedford as "hydrogen sulfide-polysulfide" accelerators. Their action depends on the presence of hydrogen sulfide and, therefore, on the presence of the non-rubber constituents of the rubber, in so far as the accelerators themselves do not react with sulfur to form ammonia and hydrogen sulfide at vulcanization temperatures. In this group are classified all organic bases and such compounds as form bases, as for example, aldehyde-ammonia, ethylidine-aniline, and anhydroformaldehyde-aniline.

In contrast to this class of "hydrogen sulfide-polysulfide" accelerators is that designated by Scott and Bedford as "carbosulfhydryl-polysulfide" accelerators. To this class belong all compounds which contain the mercapto group linked to carbon, such as, for example, thioureas (enol form), mercaptans and dithiocarbamates, as well as the disulfides such as thiuram disulfides which are formed from the dithiocarbamates by mild oxidizing agents or halogens. This class of compounds contains the sulfhydryl or mercapto group, which is capable of forming polysulfides, and the action of these compounds is therefore not dependent on the presence of hydrogen sulfide or the non-rubber constituents of the rubber.

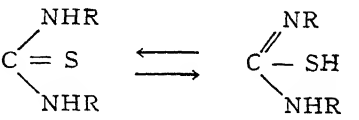
In the following paragraphs, the action of individual compounds of both classes of accelerators will be discussed in greater detail. According to Scott and Bedford, aldehyde-ammonia, hexamethylenetetramine, and para-phenylenediamine react with sulfur, forming hydrogen sulfide and ammonia (or ammonium sulfide) which, on further reaction with sulfur, produce ammonium polysulfide, the active accelerator. These three compounds, therefore, belong to a subdivision of the "hydrogen sulfide-polysulfide" class in which the activity is not dependent on the presence of the non-rubber constituents of the rubber. In opposition to the opinion that these compounds function in the same manner, are the observations made by D. F. Twiss, in collaboration with S. A. Brazier,[153] and C. W. Hawson.[154] These investigators found that the behavior of aldehyde-ammonia differed from that of hexamethylenetetramine, in rubber mixtures containing zinc oxide. While the accelerating action of hexamethylenetetramine in the presence of small amounts of zinc oxide (less than one per cent) was greatly enhanced, the influence of zinc oxide on aldehyde-ammonia was almost absent. Therefore, conditions are not so simply explained as Bedford and Scott believed them to be, especially if metallic oxides are present. In an investigation by Bedford and Scott[155] on the action of sulfur on aldehyde-amine condensation products such as anhydroformaldehyde-aniline and methylenediphenyldiamine, it was ascertained that, in addition to other urea derivatives, thiocarbanilide

[153] *J. Soc. Chem. Ind.*, **39**, 125 (1920).
[154] *J. Soc. Chem. Ind.*, **39**, 287 (1920).
[155] *J. Ind. Eng. Chem.*, **12**, 31 (1920).

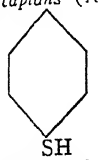
was the chief product of the reaction. Complex reactions, therefore, occur in this case and more will be said concerning them later.

In the following graphical formulas may be found types of compounds which are classified in this group:

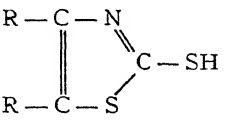
Thioureas:



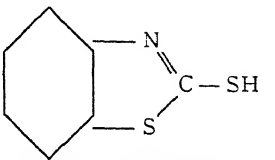
Mercaptans (R_3CSH):



thiophenols

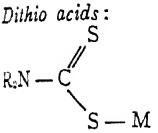


mercaptothiazoles

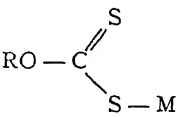


mercaptobenzothiazoles

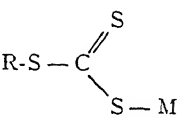
Dithio acids:



dithiocarbamates

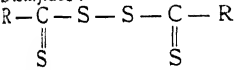


xanthates

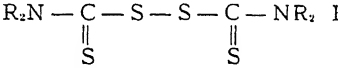


trithiocarbonates

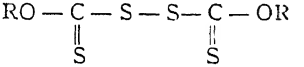
Disulfides:



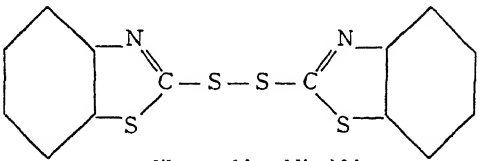
dithiodiacyl disulfides



thiuram disulfides



dixanthates



dibenzothiazyldisulfides

A glance at the above type compounds shows that for the first time organic accelerators containing no nitrogen are represented.

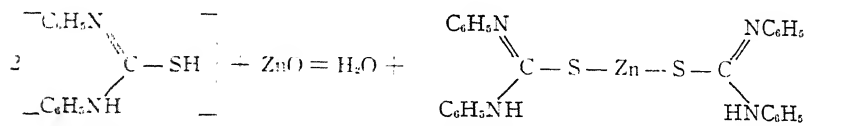
Reference has already been made to the increase in accelerating action of hexamethylenetetramine by zinc oxide. This is most decidedly the case with guanidine derivatives. Bedford and Scott assume that disubstituted guanidines such as diphenylguanidine react with hydrogen sulfide, forming ammonia and thiocarbanilide, so that we are here concerned with accelerators of both the hydrogen sulfide-polysulfide and carbosulfhydryl-polysulfide groups. The previously mentioned aldehyde-amine condensation products may be considered similar. Later, however, Bedford and Sebrell [156] were able to prove that diphenylguanidine forms an addition product with hydrogen sulfide and forms salts with mercaptans. Hence the disubstituted guanidines were again considered to be entirely of the hydrogen sulfide-polysulfide group. Incidentally, W. Scott [157] showed that, of the disubstituted guanidines, the di-ortho-tolyl derivative was the most powerful, followed by the di-para-

[156] *J. Ind. Eng. Chem.*, **14**, 25 (1922). [157] *India Rubber J.*, **64**, 476, 605 (1922).

tolyl- and finally diphenylguanidine. It would appear from this that the effect of chemical constitution should not be entirely disregarded. Scott assumed further that the activating effect of zinc oxide was due to the formation of derivatives of the type of complex zinc-ammonia compounds, zincates, or thiozincates, and that the noticeable improvement in physical properties of the vulcanizates in the presence of zinc oxide might be ascribed to physicochemical action.

Accelerators of the second class, the carbosulfhydryl accelerators, are distinguished by the grouping, $\equiv C \cdot SH$, or by their ability to form this group under the conditions of vulcanization. By means of the mercapto group, they are capable of forming salts with metallic oxides. In this class there now appear for the first time compounds which, in the absence of zinc oxide from the rubber mixture, are well-nigh inactive, while in its presence they are so activated that they are distinguished from the majority of accelerators by the title "ultra-accelerators." A. Maximoff,[158] in the years 1914-16, appears to have been the first to learn of the activating action of the metallic oxides on accelerators of this class, the dithiocarbamates in particular. In the literature, however, the activating action of zinc oxide upon certain accelerators was first established by D. F. Cranor.[159] Maximoff, as well as Bedford and Sebrell,[160] assumes that the zinc salts of these compounds are the really reactive substances with regard to accelerating action.

We will now consider the theories which have been advanced to explain the mechanism of accelerator action in the presence of zinc oxide. As already mentioned, it is not the organic substances themselves but their zinc salts that are considered to be the active agents. For certain substances, such as the disulfides, however, another view must be accepted. The formation of a zinc salt, in the case of the thioureas, is possible only if one assumes the isomeric form for their constitution, as is indicated above. Diphenylthiourea must therefore react with zinc oxide as follows:



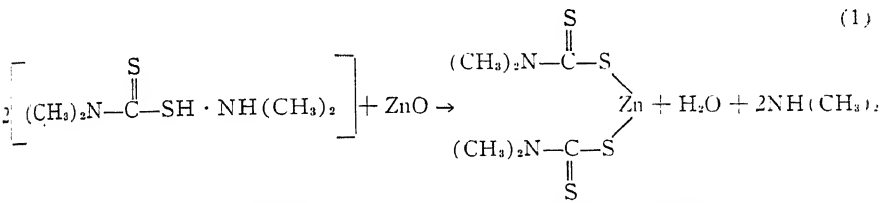
An indication of the correctness of this representation is to be had in Sebrell's observation [161] that a solution of diphenylthiourea in benzene and aniline dissolves a considerable quantity of zinc oxide, while the benzene-aniline solution alone does not. Furthermore, upon stirring with litharge, a solution of diphenylthiourea in benzene at 15° to 20° C., forms a red mercaptide which on warming is transformed into lead sulfide. Addition of sulfur to the cold, red solution of the mercaptide deepens the color. From this, then, it appears that diphenylthiourea forms salts with metallic oxides which activate sulfur by formation of polysulfides, but which are decomposed by hydrogen sulfide into mercaptans and metallic sulfides. These hypotheses are insufficient, however, for Maximoff has established in his investigations that the zinc and lead dithiocarbamates act as powerful accelerators only in the presence of zinc oxide. C. W. Bedford and H. Gray[162] believe this to be explained by assuming that the presence of zinc oxide retards the decomposition of the

[158] *Caoutchouc and gutta-percha*, **18**, 10,944, 10,986 (1921).
[159] *India Rubber J.*, **58**, 1199 (1919).
[160] *J. Ind. Eng. Chem.*, **14**, 25 (1922).
[161] Bedford and Winkelmann, "Systematic Survey of Rubber Chemistry," p. 39, Chemical Catalog Co., Inc., New York, **1923**.
[162] *India Rubber J.*, **64**, 476, 604 (1922).

organic zinc salt by hydrogen sulfide formed in the rubber compound, or else after its decomposition causes its synthesis again.

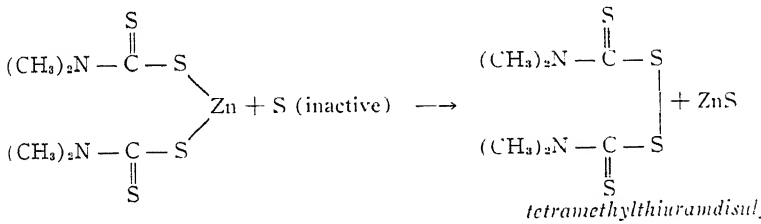
G. Bruni and E. Romani [163] also assume that accelerators of this class function through the formation of zinc salts, but in individual cases incline toward other views. Bruni [164] had already demonstrated the activity of the metallic dithiocarbamates in 1918, and that a cold vulcanization of a rubber mixture which contained sulfur, zinc oxide, and an aromatic amine would occur if it were exposed to carbon bisulfide vapors.[165] Furthermore, Romani [166] found that the oxidation product of piperidinium pentamethylenedithiocarbamate, i.e., the pentamethylenethiuramdisulfide, induced vulcanization of a rubber-zinc oxide mixture in the absence of sulfur, and that other thiuram disulfides behaved similarly. On the other hand, the activity of metallic dithiocarbamates is dependent on the presence of free sulfur. Since Bruni and Romani were able to establish the fact that thiuram disulfides are formed by the action of free sulfur on the metallic dithiocarbamates, they believed the mechanism of the reaction to be as follows:

(1)



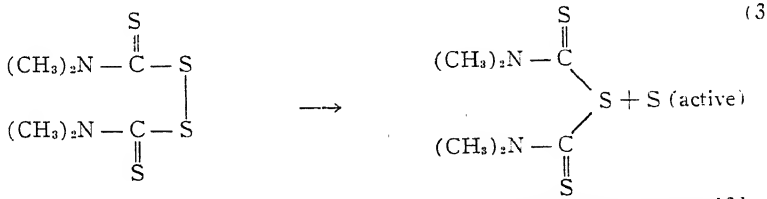
dimethylammonium dimethyldithiocarbamate *zinc dimethyldithiocarbamate*

(2)



tetramethylthiuramdisulfide

(3)

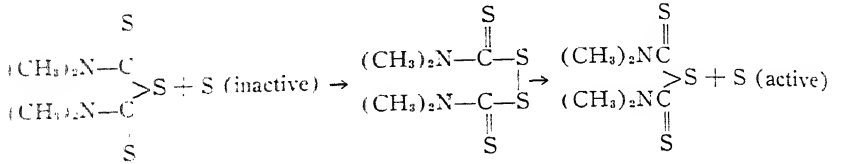


tetramethylthiurammonosulfide

Reaction 3 proceeds under the influence of the vulcanization temperature and liberates sulfur in an active form. In order to explain the fact that small amounts of this type of accelerator are sufficient to activate proportionately large amounts of free sulfur and yield normal vulcanizates, it is necessary to assume the reformation of the disulfide from the sulfide in the presence of

[163] *Giorn. chim. ind. applicata*, **3**, 351 (1921); *India Rubber J.*, **62**, 63, 89 (1921).
[164] Italian Pat., 173,322 (1918); 173,364 (1919).
[165] *Giorn. chim. ind. applicata*, **3**, 196 (1921).
[166] *Giorn. chim. ind. applicata*, **3**, 197 (1921).

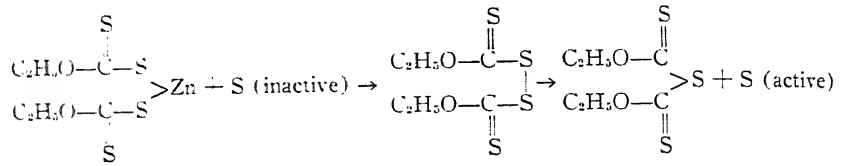
free (inactive) sulfur, and also that this reaction takes place at vulcanization temperature.



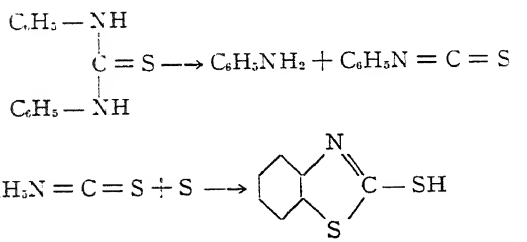
The action of accelerators of this type would not be dependent on the presence of zinc oxide.

We see, therefore, that the theories of Bedford and Scott or Sebrell and those of Bruni and Romani are similar. Both assume the intermediate formation of zinc salts, but whereas Bedford and his co-workers attribute the activation of the sulfur to polysulfide formation, Bruni and Romani consider the formation of disulfides to be responsible.

According to the disulfide theory, the action of the zinc alkyl xanthates would be explained by the following equation:



To the above reactions must be added one in which the activating agent, either the disulfide or a similarly acting substance, is regenerated. Bruni and Romani also attribute the accelerating properties of diphenylthiourea and its analogs to disulfide formation, assuming the intermediate formation of phenyl mustard oil:



In support of this mechanism, Bruni and Romani point out that tetra-substituted thioureas do not act as accelerators, since they are not capable of forming phenyl mustard oil. This fact, however, can also be claimed by

Bedford and his co-workers, as evidence for their theory on the ground that, since these compounds are tetra-substituted, the capacity for enolization is absent and they cannot form the mercaptan group which is necessary for the formation of polysulfides.

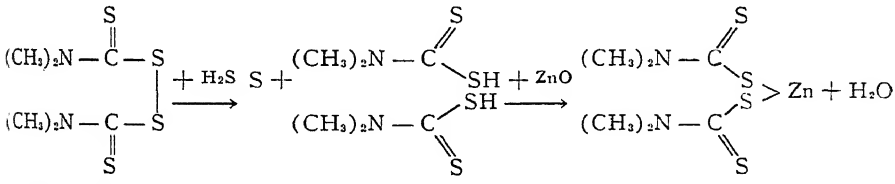
A new accelerator theory [*Kolloid-Z.*, **59**, 373 (1932)] has recently been proposed by Ditmar to explain the action of thiazoles.* The theory is applicable to thiazoles in the presence of ZnO but not to thiazole salts. According to this theory the S_8 forms active atomic sulfur at vulcanization temperatures. The active sulfur, e.g. oxidizes the 2-mercaptobenzothiazole with the formation of H_2S. Simultaneously the active sulfur reduces the ZnO present to zinc with the formation of ZnS and SO_2. The zinc unites with the thiazole rest to form the zinc salt. The hydrogen sulfide and sulfur dioxide then react as in the Peachey process to form the active vulcanizing agent thiozone, S_3.

$$SO_2 + 2H_2S \rightarrow 4H + 2O + S_3$$

The nascent hydrogen and oxygen then react with other S_8 molecules to produce active atomic sulfur or they unite with active sulfur to form H_2S and SO_2. The process is repeated until vulcanization is completed.

In the following paragraphs are presented facts which support or militate against one or the other of these two theories.

In connection with their investigation of tetramethylthiuramdisulfide, Bedford and Sebrell [167] confirmed the observation of Romani that this compound is active in the absence of free sulfur and established, furthermore, that its accelerating action is not dependent on the presence of zinc oxide. This agrees, in a way, with the expanded theory of Bruni and Romani, although the reason why the activity of the thiuram disulfide should be distinctly increased by the simultaneous presence of zinc oxide and sulfur is not explained. The following observation of Bedford and his co-workers also appears to be worthy of consideration. While tetramethylthiuramdisulfide, either with or without zinc oxide, requires higher temperatures in order to produce a vulcanizing action of any importance, rubber mixtures which contain the accelerator and zinc oxide will vulcanize at room temperature in several hours if exposed to hydrogen sulfide. Bedford believed that this phenomenon was to be explained by his polysulfide theory. He assumed that the thiuram disulfide, behaving similarly to the aromatic disulfides, was split by the hydrogen sulfide into dithiocarbamic acid and sulfur. The former, on reaction with zinc oxide, produces a salt capable of forming polysulfides.



If the mixture does not contain zinc oxide, the cold vulcanization in the presence of hydrogen sulfide does not occur. This indicates that the important thing, therefore, is not the presence of the disulfide, but the formation of the zinc dithiocarbamate. In opposition to this, however, is the fact that zinc ethyl xanthate,[168] as well as the zinc dithiocarbamates [169] are almost valueless in zinc oxide-free mixtures, while in the presence of zinc oxide they are so strongly activated that they are known as ultra-accelerators. Bedford and

* Translator's Note.

[167] *Ind. Eng. Chem.*, **14**, 25 (1922).

[168] Bruni and Romani, *India Rubber J.*, **62**, 63, 89 (1921).

[169] Maximoff, *Caoutchouc and gutta-percha*, **18**, 10,944, 10,986 (1921); Twiss, Brazier and Thomas, *J. Soc. Chem. Ind.*, **41**, 81 (1922).

Gray [170] believe, as already mentioned, that this can be explained by assuming that the excess of zinc oxide retards the decomposition of the zinc salts (which according to their theory are the sulfur activators) by hydrogen sulfide already formed in the mixture, or regenerates them if already decomposed. They believe they are justified in this assumption, since Bedford and Sebrell had established that solutions of zinc dimethyldithiocarbamate are decomposed by hydrogen sulfide. It may also be mentioned that these investigators could in no case find evidence of disulfide formation in studying the reaction of sulfur with zinc dimethyldithiocarbamate in hot xylene. It may be objected, of course, that it is doubtful whether the same reaction would take place under these conditions as in rubber. The observation made by Bedford and Sebrell, as well as by S. M. Cadwell,[171] that aniline and other aromatic amines are capable of increasing the accelerating action of metallic xanthates and dithiocarbamates as well as the corresponding disulfides, so that a vulcanization at a lower temperature is possible, is also worthy of notice. This action is ascribed to the solubility of these accelerators in the aromatic amines. A new factor influencing accelerator action enters in, therefore, insofar as the assumed explanation of the facts is correct.

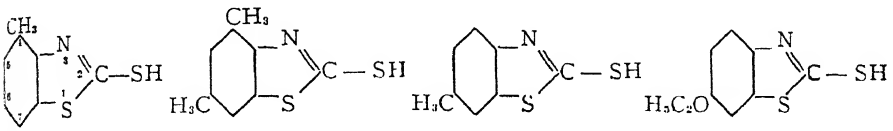
Bruni and Romani, as mentioned previously, have also traced the action of diphenylthiourea and its analogs to disulfide formation. They assume the intermediate formation of phenyl mustard oil and its reaction with sulfur, by which mercaptobenzothiazole is formed. In favor of this reasoning is the fact that mercaptobenzothiazole was found simultaneously and independently by Bedford and Sebrell [172] and by Bruni [173] to be a powerful accelerator. It was found, however, that phenyl mustard oil is not more active than thiocarbanilide, a fact which is contrary to the mechanism assumed in the Bruni and Romani theory (*see* p. 326). Furthermore, Bedford and Sebrell raise the objection that thiocarbanilide exhibits a vulcanization accelerating action at a considerably lower temperature than that required for the formation of mercaptobenzothiazole from phenyl mustard oil. Whether this objection is valid or not, cannot be decided definitely without further work, since the presence of rubber, having the ability to combine with sulfur, may influence the reaction materially.

The mercaptobenzothiazoles are acids and are capable of forming salts, especially of zinc and lead. These salts are more active than the free mercaptans, but the disulfides obtained from the mercaptans by oxidation are less active than the mercaptobenzothiazoles themselves. This is decidedly against the disulfide theory, provided that the reactions taking place in the rubber mixtures are not greatly influenced by the presence of zinc oxide. It is a fact, in any case, that all these compounds are hardly to be considered as accelerators in the absence of zinc oxide, while in its presence they are very active. A new factor, the dependence of accelerator action on chemical constitution, is brought into consideration by some very interesting work which may be considered in conclusion.

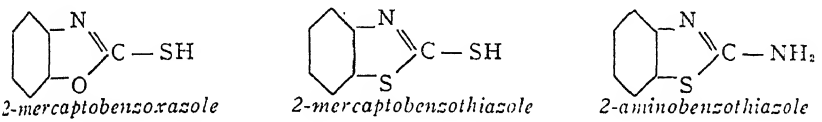
K. Gottlob [174] had already shown that, while para-phenylenediamine acts as an accelerator, the ortho and meta compounds are practically valueless, a fact which was attributed by him at that time to the differences in the dissociation constants. Kratz, Flower and Shapiro,[175] however, pointed out

[170] *India Rubber J.*, **64**, 604 (1922); *see* also G. S. Whitby; *J. Soc. Chem. Ind.*, **42**, 370 (1923).
[171] U. S. Pat., 1,440,961 to 1,440,964 (1922).
[172] *Ind. Eng. Chem.*, **13**, 1034 (1921); **14**, 25 (1922).
[173] *Atti acad. lincei*, **31** (5), I, 86 (1922).
[174] *Gummi-Ztg.*, **30**, 303, 326 (1916).
[175] *Ind. Eng. Chem.*, **13**, 67 (1921).

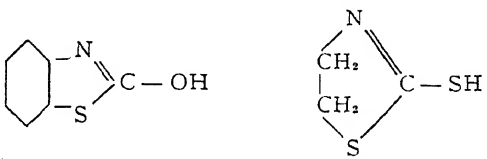
that this explanation could not hold. The constitution alone, therefore, must explain the difference in behavior of the isomeric phenylenediamines. The first comprehensive investigation of the effect of chemical constitution on accelerator action was made by L. B. Sebrell and C. E. Boord.[176] They studied the influence of alkyl groups in various positions in the benzene ring of mercaptobenzothiazole upon the accelerating action and found the 4-methyl-2-mercaptobenzothiazole to be the most powerful accelerator of this series, others ranking as given in the following order:



The activity of the unsubstituted derivative ranked it intermediate between the 4,6-dimethyl and the 6-methyl derivatives. Sebrell and Boord also studied the influence of various groups and atoms on the accelerating influence in the following compounds:

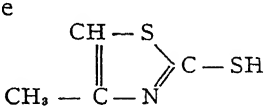


2-mercaptobenzoxazole *2-mercaptobenzothiazole* *2-aminobenzothiazole*



2-hydroxybenzothiazole *2-mercaptothiazoline*

It developed that the mercapto group was the most essential to the acceleration, followed in importance by the ring sulfur atom. The benzene ring was the least important of these three factors. The mercaptobenzoxazole was less active than the corresponding thiazole, yet more active than the aminobenzothiazole. The hydroxybenzothiazole was decidedly inferior to the mercaptobenzothiazole in activity. The mercaptothiazoline exerted a powerful accelerating action, though less than the mercaptobenzothiazole. Bruni and Romani,[177] in addition to the above, have established that 2-mercapto-4-methylthiazole



and its salts are just as active as the mercaptobenzothiazoles. This confirms the view that the benzene ring is practically without importance as far as accelerating action is concerned. Bruni and Romani vulcanized rubber-sulfur mixtures which contained 1 to 3 per cent of the thiazoles mentioned, in the presence of zinc, lead, calcium, magnesium or mercury oxides, at 120° C., for 5 minutes. The investigation showed that 2-mercapto-4-methylthiazole yielded no disulfide, but on the contrary a mono-

[176] *India Rubber J.*, **64**, 27, 476, 605 (1922); *Ind. Eng. Chem.*, **15**, 1009 (1923). [177] *Atti acad. lincei*, **31** (5), I, 86 (1922).

sulfide. It was not established whether or not the latter in turn acted as a vulcanization accelerator. Since it is not apparent why the mercaptothiazole should behave differently than the corresponding mercaptobenzothiazole under the same conditions, the monosulfide formation in the case of the former seems to be an argument in opposition to the disulfide theory of Bruni and Romani.

Ph. Schidrowitz, de Gouvea, and Osborne [178] have considered the question of variations in constitution in homologous series and found that the dimethylamine-dimethyldithiocarbamate and the diethylamine-diethyldithiocarbamate differ but slightly in their accelerating action when used alone, while on the contrary, the dimethyl compound, in the presence of zinc oxide, is more active than the diethyl derivative. Tetramethylthiuramdisulfide, however, according to Twiss, Brazier, and Thomas,[179] is a somewhat weaker accelerator than the corresponding tetraethyl derivative, so that there seems to be no rule governing the relative activity of the homologs in a given series. Furthermore, D. F. Twiss [180] established that the dithiocarbamates and thiuram disulfides derived from primary amines are in general less active than those derived from secondary amines. On the other hand, the dithiocarbamates of primary amines are less activated by zinc oxide than those derived from secondary amines. Later investigations of a systematic character by Elley and Powers [181] on the disubstituted guanidines, as well as by Naunton [182] on the activity of diarylthioureas and diarylguanidines, considered together with the already mentioned investigations of Sebrell and Boord,[183] lead to the conclusion that the accelerating action rises with advancing molecular weight of the aryl group. Electropositive substituents appear to increase the activity, electronegative groups to lower it. It is less clear, however, why with tolyl isomers of thiourea, the activity diminishes from ortho to para compound, while with the corresponding guanidines the ranking is reversed.

Neither the theory of Bedford and Scott nor that of Bruni and Romani at present gives a satisfactory explanation for these fine differences in accelerator action which have a constitutional basis. Both theories, moreover, are deficient in that they fail to explain the accelerating action of nitroso compounds. Little experimental work has been published concerning these compounds, since on account of certain undesirable properties they have been unpopular for technical use. They are poisonous in their action on the skin and discolor the vulcanizates in which they are used. Their accelerating action was discovered by S. J. Peachey, who first used para-nitrosodimethylaniline and its homologs,[184] later p-nitrosophenol and the nitrosocresol,[185] and finally nitrosobenzene.[186] They are activated by zinc oxide and magnesium oxide,[187] although with litharge [188] their activity is materially decreased. With regard to the reaction mechanism of the nitroso compounds, Scott and Bedford [189] believe that their polysulfide theory may be applied, since p-nitrosodimethylaniline can be reduced to p-aminodimethylaniline by hydrogen sulfide, and since hydrogen sulfide is formed in a rubber mixture during vulcanization. H. P. Stevens [190] had already observed, however, that this explanation, which had been offered at an even earlier date, could not be correct, since although para-nitrosophenol acts as an accelerator, its

[178] *India Rubber J.*, **64**, 75 (1922).
[179] *J. Soc. Chem. Ind.*, **41**, 86 (1922).
[180] *India Rubber J.*, **63**, 182 (1922).
[181] *India Rubber World*, **75**, 143 (1926).
[182] *J. Soc. Chem. Ind.*, **44**, 549 (1925).
[183] *Ind. Eng. Chem.*, **15**, 1064 (1923).
[184] Ger. Pat., 323,088 (1920).
[185] Ger. Pat., 328,611 (1920).
[186] Brit. Pat., 136,716 (1919).
[187] Peachey, *J. Soc. Chem. Ind.*, **36**, 424 (1917).
[188] J. L. Rosenbaum, *India Rubber J.*, **63**, 225 (1922).
[189] *J. Ind. Eng. Chem.*, **13**, 125 (1921).
[190] *India Rubber World*, **62**, 719 (1920).

reduction product, para-aminophenol, is completely inactive. Bruni and Romani [191] were just as unsuccessful in experiments in which they attempted to prove that the activity of para-nitrosodimethylaniline and its homologs fits in with their disulfide theory. They, too, were baffled by nitrosophenol and nitrosobenzene, for the activity of which they could find no satisfactory explanation. They considered it possible that the nitroso group adds to the double bond of the rubber hydrocarbon just as nitrosobenzene does to unsaturated compounds, e.g., safrole and eugenol, thus showing itself to be an accelerator which acts not by activation of sulfur but on the rubber hydrocarbon itself. According to Scott and Bedford,[192] para-nitrosodimethylaniline gives rise to sulfur dioxide and hydrogen sulfide by reaction with sulfur, so that this activation should be similar to that occurring in the Peachey process (*see* p. 334). Bedford and Sebrell [193] attributed the accelerating properties of the nitroso compounds to their oxidizing properties, which should cause a decomposition of the hydrogen sulfide formed during vulcanization. All of these hypotheses require further proof. It can be said that a satisfactory explanation of the activity of this class of accelerators does not yet exist.

Summarizing the ideas generally prevailing on the theory of acceleration of vulcanization, the following may be said:

It is assumed that accelerators transform the sulfur present in a rubber mixture to an especially active form. The accelerator, whether inorganic or organic, is supposed to act not as such, but to combine with the sulfur (in some cases after reaction with hydrogen sulfide produced in the mixture) to form products which are capable of splitting off the actual vulcanizing agents in an especially active form, regenerating a compound which is as effective in activating sulfur as the original compound. In proving these theories, organic compounds have been allowed to react with sulfur before mixing with rubber.[194] It has thus been established that certain substances become accelerators upon heating with sulfur. When used without having been previously heated with sulfur, they were not accelerators, since the temperature required for their reaction with sulfur lay above that normally used for vulcanization.

The inorganic accelerators are supposed to act by forming metallic salts with fatty acids and esters contained in the rubber resins. These salts must be soluble in the rubber and in this condition are capable of acting as sulfur activators. The same applies to organic accelerators which require activation by metallic oxides. The fact that these organic-metallic compounds require excess metallic oxide to make them powerful accelerators is explained by assuming that the excess oxide prevents the decomposition of the metallic salt by hydrogen sulfide formed in the mixture or by other acidic products resulting from decomposition of certain accelerators. If the decomposition of the metallic salt is not absolutely prevented by excess oxide, it may be assumed to be regenerated by this excess oxide. According to certain information which has been obtained,[195] organic fatty acids contained in the rubber resin increase the activity of organic accelerators in the presence of metallic oxides by increasing the surface of the oxide, through chemical reaction, making it react more readily with the accelerator, and thus developing its full activity. The importance of the degree of dispersion of a metallic

[191] *Giorn. chim. ind. applicata*, **3**, 351 (1921).
[192] *J. Ind. Eng. Chem.*, **13**, 125 (1921).
[193] *J. Ind. Eng. Chem.*, **13**, 1034 (1921).
[194] Brit. Pat., 130,857 (1919).
[195] *Cf.*, for example, B. G. Martin and S. Davey, *J. Soc. Chem. Ind.*, **44**, 317 (1925).

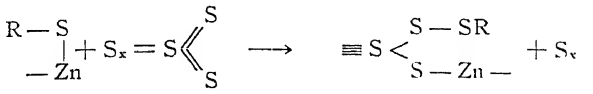
oxide may be seen from the fact that (contrary to the usual action of the average zinc oxide), zinc oxide may act as a vulcanization promoter in the absence of organic accelerators if a particle size of 0.15 μ is not exceeded and its acidity is not greater than 0.1 per cent.[196] The reactivity of zinc oxide can be increased if it is not used in the calcined form but as a hydrate with 0.1 to 1.85 mols of water to 1 mol of zinc oxide.[197]

While the previously described theories base the acceleration of vulcanization on an activation of sulfur, there are also theories which postulate that the accelerators act on the rubber itself. M. Le Blanc and M. Kröger[198] showed that the viscosity of a rubber solution decreases with increasing dielectric constant, and that by addition of an accelerator it suffers a further diminution. Similar observations were later made by G. S. Whitby,[199] who found that the viscosity of a rubber solution in water-free benzene is perceptibly decreased by very small amounts of organic bases. Similar investigations have led W. J. S. Naunton[200] to a method of quickly determining the vulcanization-promoting properties of organic compounds soluble in benzene, by determining their influence on the viscosity of a benzene solution of rubber. Substances which accelerate vulcanization lower the viscosity of the solution. These observations led Whitby[201] to believe that accelerators, insofar as they are bases or produce bases on decomposition, form salts (soaps) with the acids of the rubber resins, which, as the alkali soaps, act as accelerators by increasing the degree of dispersion of the rubber. Twiss[202] had already expressed similar views in regard to the accelerating action of alkalies. In this connection there should also be mentioned the observation made by M. Kröger[203] according to whom the rate of reaggregation of raw rubber is considerably increased by addition of piperidine. While a sample of pure rubber withstood a load of 10 kg. after 1½ years storage, similar test pieces containing piperidine, and aged under the same conditions required a load of 17 kg. for the same elongation. It is noteworthy that this action of piperidine on the rubber is opposite to that observed on rubber in solution.

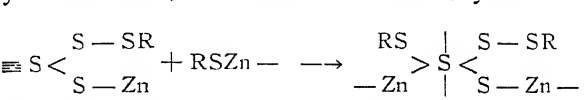
The last-mentioned hypothesis of Whitby, although in opposition to the purely chemical theories of accelerator action, is based to some extent upon the peculiar colloid chemical properties of rubber. H. Feuchter's[204] attempt to explain the process is still more elaborate. In contrast to Bedford and Bruni, who divide the accelerator action into three stages, (polysulfide or disulfide formation, splitting off of active sulfur, combination of sulfur with the rubber), Feuchter assumes in his ortho-thiozonate theory a single vulcanization reaction in which the formation of a compound (by chemical valence forces) of the crystalloidal solid phase of any of the accelerator classes with the colloidal rubber phase takes place through thiozonide sulfur. It is assumed that for the acceleration of vulcanization, two substances must be present. These are denoted by Feuchter as the "accelerator" (with acid function) and the "activator" (such as a salt-forming oxide or a base). These form the "accelerator system." The "carbosulfhydryls," which correspond to the carbosulfhydryl-polysulfide accelerators of Bedford and Scott, can serve

[196] Brit. Pat., 213,454 (1923).
[197] Brit. Pat., 239,173 (1923).
[198] *Z. Elektrochem.*, **27**, 335 (1921).
[199] *India Rubber World*, **69**, 795 (1924).
[200] *J. Soc. Chem. Ind.*, **44**, 243 (1925).
[201] *Ind. Eng. Chem.*, **15**, 1008 (1923).
[202] *J. Soc. Chem. Ind.*, **36**, 782 (1917).
[203] *Gummi-Ztg.*, **40**, 2429 (1926).
[204] *Kolloidchem. Beihefte*, **20**, 90 (1924). *Cf.* Kratz, Flower, and Coolidge, *Ind. Eng. Chem.*, **12**, 321 (1920).

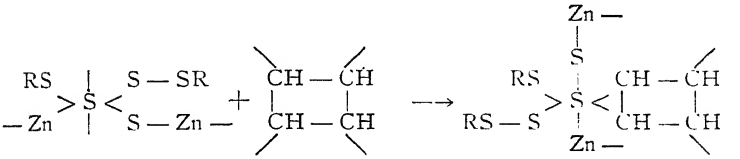
as "accelerators" and with zinc oxide as "activator" form the mercaptides for the vulcanization reaction. The "carbohydroxyls" (alcohols, aldehydes, carboxylic acids) can also serve as "accelerators" with activators, such as the alkali hydroxides, magnesia, ammonia and its derivatives, and lead oxide. Furthermore, Feuchter differentiates between "simple" and "multiple-activated" acceleration. "Simple" acceleration proceeds through the formation of accelerator thiozonides by the action of salt-like combinations of accelerator and activator on the sulfur, after double dissociation of the reaction components has occurred.



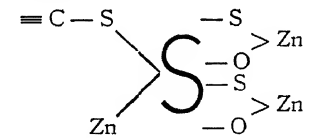
The primary thiozonide, on further reaction, yields the secondary thiozonide,



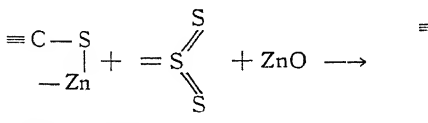
which forms the vulcanizate on reaction with "polyprene."



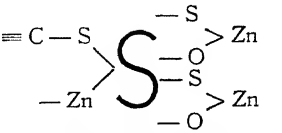
This "simple" acceleration can be increased by metal oxides or amines. The "multiple-activated" acceleration is explained by Feuchter on the principle of "multiple atomic loading." The potential activators such as zinc oxide, magnesia, amines, etc., are supposed to fix the thiozonate and form the extraordinarily reactive ortho-thiozonates of the type



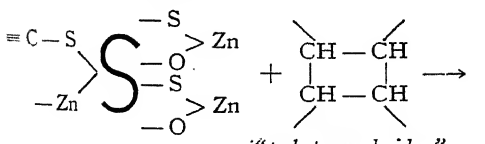
which are the real accelerators of the multiple vulcanization acceleration. With zinc mercaptide as the accelerator system and zinc oxide as the potential activator, a reaction scheme such as the following results:



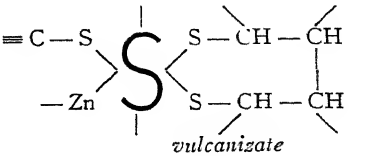
zinc mercaptide



zinc ortho-thiozonate



"polyprene bridge"



vulcanizate

The "polyprene bridge" is a part of Feuchter's rubber molecule "which consists of a large closed ring, the individual members of which are eight-membered carbon rings which are bound doubly at opposite sides by carbon atoms of the polyprene bridge." The vulcanizate consists of the accelerator components and the polyprene components bound together by valence bonds. The accelerator components, in accordance with their salt-like nature, form an extremely fine solid network, a crystal-net, while the polyprene components remain in a highly viscous condition. This crystalline network of the accelerator component is supposed to correspond somewhat to the crystalline phase of ordinary gels. However, because of the restrictions on crystallization, imposed by the highly viscous polyprene mass in the crystal-net of the vulcanizate, a much higher amount of potential energy remains as an inner tension, which manifests itself externally as elasticity.

With regard to their technical activity, the organic accelerators may be divided into the four classes listed below.[205]

1. *Ultra-accelerators.* Examples: dithiocarbamates and xanthates used with zinc and zinc oxide. Vulcanization temperature: considerably below 100° C. Vulcanization period: a few minutes.
2. *Rapid accelerators.* Examples: diphenyl- and di-o-tolylguanidines, thiuram disulfides. Vulcanization temperature: above 100° C. up to about 140° C. Vulcanization period: 20 to 40 minutes.
3. *Moderate accelerators.* Examples: aldehyde-ammonia, hexamethylenetetramine. Vulcanization temperature: 142° C. Vulcanization period: approximately 60 to 90 minutes.
4. *Slowly acting accelerators.* Examples: thiocarbanilide, formaldehyde-aniline, triphenylguanidine. Vulcanization temperature: 142° C. Vulcanization period: approximately 90 to 120 minutes.[206]

Other Kinds of Vulcanization

The Peachey Process

In an investigation of the behavior of rubber with various forms of sulfur, S. J. Peachey and A. Skipsey[207] found that the type of sulfur formed momentarily by reaction of sulfur dioxide and hydrogen sulfide combines quickly with rubber at room temperature, bringing about vulcanization. It is to be noted, however, that the vulcanization takes place only if the reaction of the gases occurs in the immediate presence of the rubber hydrocarbon. The sulfur is active only at the instant of its formation and Peachey and Skipsey assumed, therefore, that the activity of the sulfur is due to its atomic condition. Bedford and Sebrell[208] believe, on the other hand, that the intermediate formation of trithiozone is the important factor.*

[205] F. Kirchhof, "Fortschritte der Kautschuk-Technologie," p. 154, Dresden, **1927.**

[206] *See* also p. 368, and "Technical Data on Accelerators," by N. A. Shepard and J. E. Whittenberg in "The Vanderbilt Rubber Handbook," p. 88, R. T. Vanderbilt Co., New York, **1932.**

[207] *J. Soc. Chem. Ind.*, **40**, 5 (1921).

[208] *J. Ind. Eng. Chem.*, **14**, 29 (1922).

* Translator's Note. According to recent studies of P. Bary [*Rev. gén. caoutchouc*, **8**, No. 71, 25 (1931)] the vulcanization of rubber with SO_2 and H_2S depends upon the high state of dispersion of the sulfur in the rubber and not upon the formation of colloidal sulfur.

The new process, which has found commercial application, is carried out by exposing the already-formed rubber articles alternately to hydrogen sulfide and sulfur dioxide. The gases diffuse into the rubber easily and produce the highly reactive form of sulfur. According to Peachey, the vulcanizates obtained are entirely equivalent, with regard to mechanical properties, to those obtained using the hot vulcanization methods. They are even superior to the latter, since in this type of vulcanization the disaggregating effect of heat is entirely avoided. The process, which, however, is applicable only to thin rubber articles, is conducted commercially as follows: the rubber or the rubber mixture is exposed for 10 minutes to the action of sulfur dioxide gas. A brief exposure to air follows to remove the gas adsorbed on the surface, and then the article is exposed for 20 to 30 minutes to hydrogen sulfide. An advantage to be emphasized in the use of this process is the fact that organic pigments, coal-tar dyes, or natural dyes such as chlorophyll, which suffer decomposition by heat or by the action of sulfur chloride, can be used in rubber compounding. Peachey and Skipsey showed that the new process might also be used for vulcanization in solution. If rubber solutions in benzene or gasoline are saturated with hydrogen sulfide and then mixed with a solution of sulfur dioxide in the same solvent, gelation occurs in a few minutes, and well-vulcanized rubber remains after removal of the solvent by evaporation.

A process which probably depends on reactions similar to those which occur in the Peachey process has been patented [209] by the Société Française du Caoutchouc Mousse. A cold vulcanization is claimed to result on treatment of rubber or rubber solutions with hydrogen sulfide and chlorine, if desired, with the addition of accelerators and pigments.

Use of Nitro-Compounds and Peroxides

It is only natural that many attempts have been made to discover substances which can replace sulfur as a vulcanizing agent. J. Ostromislensky has been the principal investigator in this field.[210] He sought compounds which, like sulfur, are capable of oxidizing ethylene derivatives or of adding to double bonds, and the physical constants of which correspond to those of sulfur. He believed that he had found such substances in the nitro compounds, and reported that various nitro compounds could vulcanize synthetic rubber or natural rubber even more easily and more quickly than sulfur. He declared that the properties of the products thus obtained were essentially the same as those obtained by vulcanization with sulfur. The vulcanization experiments included the use of nitrobenzene, di- and trinitrobenzene, tri- and tetranitronaphthalene, picramic acid, picric acid, picryl chloride, artificial musk, nitrocyclohexane, etc. It appeared that no relationship existed between the capacity of the substances for adding to a double bond and their vulcanizing ability. For example, picramic acid adds to ethylene derivatives much more readily than other nitro compounds, while in vulcanizing ability it is surpassed by most of them.

Rubber can be vulcanized most easily in the presence of 1,3,5-trinitrobenzene, followed by dinitrobenzene, nitrobenzene and tetranitro-

[209] French Pat., 559,346.

[210] *J. Russ. Phys. Chem. Soc.*, **47**, 1453, 1462, 1467, 1885, 1898, 1904 (1915).

naphthalene. Unsatisfactory results were obtained with picric acid and picryl chloride, while with tetranitromethane a vulcanization could not be brought about. Similarly, triphenylmethane and diaminotriphenylmethane failed to cause vulcanization, although the ease with which they add to double bonds is known. Ostromislensky concluded, therefore, that the possibility of vulcanization with nitro compounds depended on the ability of an active oxygen atom of the nitro group to add to the double bond, since the nitroso and iso-nitroso compounds do not act as vulcanizing agents for rubber. With regard to the mechanism of the vulcanization, Ostromislensky made the following representation: It begins with a chemical reaction, whereby very small amounts of rubber react with the vulcanizing agent, these small amounts being indispensable to the success of vulcanization, however. The further course of the vulcanization is a physical reaction between the small amounts of changed rubber and the unchanged portions. The process occurs in two steps, therefore: (1) in which a chemical reaction of a small amount of rubber occurs and (2) in which the adsorption or swelling of the unchanged rubber in the reaction product of the first step takes place (*see* p. 299).

Ostromislensky established in addition, that metallic oxides which promote vulcanization with sulfur, perform the same service for the nitro compounds. They may be listed in the order of their activity in this process, as follows: litharge, zinc oxide, lime, magnesia, barium oxide; litharge being the most active. In contrast to their action in sulfur vulcanization, mixtures of primary and secondary amines retarded vulcanization with nitrobenzene and reduced the technical value of the vulcanizates.

If Ostromislensky's picture of the process is correct, i. e. that an active oxygen atom of the nitro group is the important factor, then rubber should be capable of vulcanization with peroxides also. The investigator claimed this to be the case, since the vulcanization proceeded more easily and more quickly with benzoyl peroxide than with sulfur or the nitro compounds. The metal oxides were of no value in this case, being even detrimental. Organic accelerators and mixtures of metal oxides with amines retarded vulcanization with peroxides. In place of benzoyl peroxide, perbenzoic acid may be used, but barium peroxide is unsuited for use as a vulcanizing agent, since it splits off oxygen with sufficient velocity only at high temperatures.

Ostromislensky went still further and investigated the vulcanization of rubber with molecular oxygen, ozone, and the ozonides of organic compounds. With the aid of ozone or rubber ozonide he produced hard or soft rubbers, depending on the concentration of the vulcanizing substance. Moreover, by long action of ultra-violet light on pure rubber in dry air, a gradual vulcanization was found to occur. The process proceeded more rapidly at 40° to 80° C., while at 120° C. the rubber became oxidized and was transformed to a sticky, viscous mass. Ostromislensky also recorded the observation that damp rubber became coated in air with a slightly elastic substance which, if milled into the rubber on cold rolls, followed by heating with exclusion of air, caused a vulcanization of the unchanged internal portions of the mass. When this surface layer was removed before milling and heating, the rubber did not vulcanize.

Naturally, these communications by Ostromislensky aroused the inter-

...t of rubber technologists, and corroboration of his claims was desired. ...l. P. Stevens [211] was the first to undertake this task. He carried out ...xperiments with di- and trinitrobenzene, as well as with benzoyl perox...de. With the first-mentioned substances he succeeded in producing ...atisfactory results only when litharge or magnesia were included in the ...ubber mixture. With regard to their physical properties, the products ...ere of comparatively inferior quality. The best vulcanizates, though ...ways inferior to the products obtained with sulfur, were obtained ...ith a mixture containing trinitrobenzene 4 parts, rubber 100 parts, and ...tharge 8 parts. On the other hand, the products obtained with benzoyl ...eroxide resembled those in which sulfur was used, with regard to ...hysical properties. The amount of benzoyl peroxide required for com...lete vulcanization of the rubber was very nearly equal to the amount ...f sulfur required, but the vulcanization with the former material pro...ceeded more rapidly than with the latter. Complete vulcanization was ...eached with benzoyl peroxide (4 to 6%) at 130° to 150° C. in 10 to 15 ...inutes, whereas with 5 to 6 per cent of sulfur the vulcanization had ...carcely begun in so short a period, and the complete vulcanization re...uired 2 to 3 hours.*

A criticism of Ostromislensky's work is, that the degree of vulcani...ation attained with the nitro compounds or peroxides was not estab...ished by determination of the mechanical (physical) properties of the ...ulcanizates. Instead, the extent of vulcanization was recorded only by ...uch expressions as "incomplete," "nearly complete," "complete," etc. This gap was filled by E. Bunschoten,[212] who made possible for the first ...ime an evaluation of the new method of vulcanization. Like Stevens, Bunschoten failed to obtain satisfactory results with mixtures of raw rub...er and nitro- or metadinitrobenzene in the absence of metal oxides. After ...ulcanization periods of 30, 60, and 90 minutes in an oil bath at 147° C., the ...roduct was not in the least vulcanized and was soluble in benzene. Mixtures containing 100 parts of rubber, 4 parts of dinitrobenzene and 1 ...art of "Accelerene" or acetaldehyde-ammonia did not appear to be vul...anized after heating for periods of ½, 1, 1½, 2, 2½, and 3 hours at 147° C. However, in the presence of metal oxides, phenomena occurred which ...ere very similar to vulcanization. Slowly vulcanizing crepe and rapidly ...ulcanizing sheet rubbers were used. The mixtures consisted of 100 ...arts of rubber, 8 parts of litharge, and 4 parts of nitrobenzene. The vul...anization temperature in the autoclave was 147° C. The data obtained ...re given in Table 13.

TABLE 13.—*Vulcanization with Nitrobenzene.*

Time of vulcanization in minutes	Smoked Sheets: Tensile strength kg./cm.²	Smoked Sheets: Elongation per cent	First Latex Crepe: Tensile strength kg./cm.²	First Latex Crepe: Elongation per cent
30	0.5	697	Not sufficiently vulc.	
45	14.5	982	" "	"
60	20.4	906	" "	"
90	35.8	825	10.4	610
120	27.8	874	22	704

[211] *J. Soc. Chem. Ind.*, **36**, 107 (1917).

* Translator's Note. The vulcanization of rubber with benzoyl peroxide has recently been reinvestigated. An explanation of the mechanism of vulcanization with benzoyl peroxide has also been attempted. *See*, Van Rossem, Dekker and Prawirodipoero [*Kautschuk*, **7**, 202-204, 220-223 (1931); *Rubber Chem. Tech.*, **5**, 97 (1932)].

[212] *Kolloid-Z.*, **23**, 25 (1918).

Vulcanization had occurred, therefore, even though the tensile s was considerably lower than that found in vulcanizates containing sulfur. As judged by appearance and by the shape of the stress-strain curves, it was recognized that all the vulcanizates were of an under-vulcanized character. They were insoluble in benzene, though they swelled greatly. It is of interest that smoked sheet rubber which vulcanizes more rapidly with sulfur than do the other rubbers, showed the same behavior in this and the following experiment.

In a second series of experiments in which m-dinitrobenzene was used in place of nitrobenzene, products were obtained which no longer exhibited the property of swelling in benzene. They possessed the physical properties given in Table 14.

TABLE 14.—*Vulcanization with*

Time of vulcanization in minutes	Smoked Sheets		First Latex Crepe	
	Tensile strength kg./cm.²	Elongation per cent	Tensile strength kg./cm.²	Elongation per cent
10	103	798	.....	.....
15	105	737	82.5	742
25	87	663	79.5	675
30	92	741	86	742
45	62.5	662	73.5	641
60	51	640	73.5	629
75	52.5	616	74	622
90	39.5	515	59.5	603
120	13.4	352	58	612

Further experiments showed that increased concentrations of dinitrobenzene and litharge resulted in increased rates of vulcanization. Higher temperatures produced the same effect, just as in vulcanization with sulfur. On the contrary, the temperature seemed to have no effect on the mechanical properties of the vulcanizate. It was conclusively shown that the new process could in no case replace vulcanization with sulfur. The mechanical properties of the dinitrobenzene-litharge vulcanizates are impaired so quickly that a practical application is not to be considered. After one month's aging, Schopper test rings of vulcanizates containing dinitrobenzene and litharge, which originally had a tensile strength of 40 kg./cm.² could be broken easily by hand. These phenomena do not appear to be due to oxidation, since the acetone extract had not increased after six months' aging, and the products also remained insoluble in benzene. Bunschoten was not able to produce hard rubber by this method.[213] In order to investigate Ostromislensky's hypothesis that his process of vulcanization was based on oxidation, Bunschoten mixed into rubber various inorganic oxidizing agents, including arsenic acid, potassium persulfate, chloride of lime, potassium bichromate, potassium permanganate, potassium chlorate, potassium nitrate, sodium nitrate, pyrolusite, and potassium ferricyanide. He used four grams of each of these per 100 grams of rubber and vulcanized the mixtures for one-half hour and one hour at 147° C. in an oil bath. All the experiments resulted in products similar to slightly vulcanized rubber, but all these products dissolved after standing a few days in benzene.

[213] H. L. Fisher and A. E. Gray [*Ind. Eng. Chem.*, **20**, 294 (1928)] were able to show that the "vulcanization" with polynitrocompounds and benzoyl peroxide has no influence on the unsaturation of the rubber hydrocarbon.

Bunschoten's investigations of the influence of nitrobenzene and dinitrobenzene on the viscosity of rubber solutions are of interest. With one gram of rubber and 400 mg. of dinitrobenzene in 100 cc. of benzene, the viscosity decreased greatly when the solution stood in daylight. On standing in the dark, however, the viscosity rose. If such a solution was heated, the viscosity increased, but in the light it again decreased rapidly. Vulcanization with dinitrobenzene appears, therefore, to have an influence on the degree of aggregation of the rubber. Whether the discovery of Ostromislensky can be called true vulcanization or not, in view of the very rapid decline in the mechanical properties of the product, remains undecided according to our present knowledge of the subject. F. Kirchhof[214] calls the products, "pseudo-vulcanizates."

Use of Selenium

Since Ostromislensky had tried to substitute oxygen or oxygen-containing compounds for sulfur, it was logical to determine whether the sulfur-like element, selenium, had possibilities as a vulcanizing agent. C. R. Boggs[215] undertook to do this, and established the fact that amorphous selenium in the presence of accelerators yielded a vulcanizate in about twice the usual period of time required with sulfur at 135° C. The product had the same tensile strength and elongation as obtained with sulfur. It showed no irregular behavior with regard to electrical properties, but appeared to resist deterioration by aging better than the vulcanizate obtained with sulfur. I. Williams[216] checked these results and established, furthermore, that selenium by itself is almost completely insoluble in rubber. This is partly due to the fact that its high melting point prevents it from being melted and introduced into the rubber in this way. On the other hand, when melted with sulfur, with which it is miscible in all proportions, it forms a eutectic mixture, melting at 106° C., containing 40 atomic per cent of sulfur. Such mixtures may be easily incorporated in rubber. The experiments proved that, when used with sulfur, selenium behaves as an accelerator, only small percentages combining with the rubber. Used alone, selenium produced no vulcanization, but in the presence of organic accelerators, brought about good vulcanization. Williams was undecided whether it acted only as accelerator, or whether it exerted a specific action. That the latter alternative is to be preferred was shown later by Bierer and Davis,[217] who found that small amounts of selenium in mixtures containing reclaimed rubber increased the abrasion resistance considerably.* A mixture was used containing 46 parts of smoked sheets, 10 parts of reclaim, 21 parts of carbon black, 13.5 parts of zinc oxide, 5 parts of mineral rubber, 1.5 parts of mineral oil, 2 parts of sulfur and 1 part of ethylidine-aniline as accelerator (mixture *A*). A second mixture *(B)* was made in which the sulfur was raised to 2.5 parts; a third *(C)* contained 0.5 part of selenium added to the basic recipe; while the fourth *(D)* contained 1.25 parts of selenium. Vulcanization was

[214] "Fortschritte in der Kautschuk-Technologie," p. 90, Dresden, **1927**.
[215] *J. Ind. Eng. Chem.*, **10**, 117 (1918).
[216] *Ind. Eng. Chem.*, **15**, 1019 (1923).
[217] *India Rubber J.*, **71**, 565 (1926).
* Translator's Note. *See also*, H. Rimpel, *Kautschuk*, **7**, 94 (1931); W. Esch, *ibid.*, **7**, 190-194 (1931).

carried out at 142° C. The relative values for resistance to abrasion are given in Table 15.

TABLE 15.—*Influence of Selenium on Abrasion Resistance.*

Vulcanization Time in Minutes	Mixture A	B	C	D
20	34	48	81	90
30	57	63	89	97
45	64	72	90	86
60	63	72	72	55

The use of selenium has reached a certain importance in the manufacture of rubber goods because of this property.

A possible explanation of the improvement of the abrasion resistance by selenium has been offered by F. Kirchhof,[218] who states that in his experiments with "Vandex," a commercial selenium preparation, an addition of 1.5 per cent of the substance hardly altered the density of an unvulcanized mixture. The density of the vulcanizate was raised 2 per cent by such an addition. On the other hand a contraction in volume or increase in density of 0.5 per cent was observed on vulcanization of a similar mixture containing no selenium. It appears from this observation, therefore, that the improvement in abrasion resistance is connected with an increase in compactness of the rubber compound under the influence of the selenium.

USE OF SELENIUM MONOCHLORIDE AND SULFUR THIOCYANATE

Attempts have been made to replace not only sulfur which is used for hot vulcanization, but also the extremely disagreeable and unhealthy compound, sulfur monochloride, which is used for cold vulcanization. H. Klopstock[219] established the fact that selenium and tellurium halides add to the double bond, and that selenium monochloride induces precipitation of rubber from its solutions. M. Le Blanc and M. Kröger [220] used a solution of sulfur dithiocyanate, or when necessary with the addition of sulfur monothiocyanate and free thiocyanogen. The free sulfur dithiocyanate $S(CNS)_2$ is obtained by decomposition of potassium thiocyanate with sulfur dichloride. Since this compound is only slightly soluble in carbon disulfide, a mixture of sulfur monothiocyanate $S_2(CNS)_2$ and sulfur dithiocyanate is used. According to the statements of the investigators, the vulcanizate is distinguished from those obtained with sulfur mono- or dichloride by greater durability.

PHYSICAL VULCANIZATION

Further attention is directed to a phenomenon which Le Blanc and Kröger [221] call physical vulcanization. They observed that raw rubber at a low temperature (-50° C.) shows an elastic behavior similar to that of vulcanized rubber at room temperature. In the case of raw rubber, for each stretching temperature there corresponds a definite contraction temperature (at which the elongation is practically completely recovered). Thus for a stretching temperature of -30° C., a temperature of about + 10° C. is the contraction temperature. Within this temperature interval a certain rigidity prevails. On vulcanization, this interval is progressively decreased, until the

[218] *Gummi-Ztg.*, **42**, 529 (1927).
[219] Ger. Pat., 260,916 (1913).
[220] Ger. Pat., 408,306; 409,214 (1925).
[221] **33**, 267 (1923); **37**, 205 (1926).

fully vulcanized condition is reached when it has disappeared entirely. Le Blanc and Kröger believe that the combination of the rubber with the sulfur serves only to make the characteristic properties of raw rubber existing at 150° C. capable of existence at a higher temperature. These hypotheses are concerned only with the physical aspect of vulcanization, the importance of which can not be ignored, but they do not concern the other changes which raw rubber undergoes on vulcanization.

The investigations of H. Pohle [222] are concerned with similarities of the reinforcing action of carbon black with the vulcanizing action of sulfur. Just as one may, with a rubber mixture having a high content of sulfur, raise the tensile strength and hardness of the vulcanizate through longer vulcanization one may also increase these properties by increasing the content of carbon black. To be sure, much larger amounts of carbon black are required than of sulfur. The amount of gas black required depends on the degree of dispersion, since the more highly dispersed the black is, the more closely it approaches the action of sulfur. The same criticism applied above to the experiments of Le Blanc and Kröger, applies here also. It may be added, however, that without doubt the strengthening action is explainable by surface forces, since according to recent theories they are of great importance; for example, in the lubrication of surfaces in contact with each other.

In conclusion, the treatment of rubber with halogens and halogen compounds may be mentioned. Ostromislensky [223] believes that vulcanization may be possible here also. He reports that bromine and iodine change rubber to an ebony-like substance and that one can effect vulcanization of rubber by treatment with rubber chlorides, bromides, and iodides, with cauprene chloride and bromide, and with rubber hydrochloride, but not with aluminum chloride. Ostromislensky worked raw rubber rolled out in thin sheets with the vulcanizing substances on cold rolls, and then heated the homogeneous mixture in iron molds in the absence of air. By using the rubber halides he obtained no soft rubber products, but on the contrary fairly hard ones. By using rubber hydrochloride (1650 parts to 100 of rubber) he is supposed to have produced a product which at about 150° C. possessed all the properties of soft rubber. In this work, as in that reported previously (*see* p. 337), no exact data on the mechanical properties of the products obtained were given. Hopkinson [224] has found that chlorination of rubber which was precipitated from latex on kieselguhr, could be used to obtain hard rubber-like masses, which could be molded in forms, either with or without addition of rubber or naphtha, etc., to form rubber articles. A process of T. A. Edison,[225] in which crepe rubber cut in thin strips is treated in suitable vessels with dry chlorine and carbon tetrachloride vapors, is carried out similarly. The soft, syrupy mass which is formed is washed with water to remove hydrochloric acid, and a mixture of this chlorinated rubber and naphthalene is formed into sheets under heat and pressure. The formation of hydrochloric acid is evidence that the chlorination is not comparable to vulcanization. Vulcanization is, as far as it may be considered a chemical reaction, an addition reaction, while by the action of chlorine on rubber, substitution as well as addition, and possibly even cyclization, take place. The so-called vulcanizates are hardly to be compared with hard rubber, therefore; much less with soft rubber, in which the molecular condition is of so great importance for the physical properties.

[222] *Kolloid-Z.*, **38**, 75 (1926); **39**, 1 (1926).
[223] *J. Russ. Phys. Chem. Soc.*, **47**, 1898 (1915).
[224] Brit. Pat., 201,898 (1923).
[225] U. S. Pat., 1,495,580 (1924).

Although the investigations for the purpose of replacing sulfur or sulfur monochloride are interesting, since they widen our knowledge of the behavior of rubber, none of them except the Peachey process has been put forth on a commercial basis. It remains uncertain in the present state of our knowledge concerning them, whether any of these processes, particularly those of Ostromislensky, exactly parallel real vulcanization, for the products obtained, aside from their physical properties, differ markedly in other respects from true vulcanizates (*see* footnote p. 338).

Regeneration and Replasticization of Vulcanizates (Reclaiming)

By regeneration (reclaiming) is meant the conversion of rubber which has already been converted into vulcanized goods and used as such, into a crude rubber-like condition in which it is suitable for the manufacture of new goods, either alone or with new rubber. As long as one interpreted vulcanization exclusively as a chemical reaction, without considering the molecular condition of the rubber, it appeared self-evident that a complete desulfurization of once vulcanized material and thereby a recovery of crude rubber (i.e. a true regeneration) must lie within the realm of possibility, since all chemical reactions are reversible. However, numerous attempts to extract the chemically combined sulfur of vulcanizates and to arrive at a practical, useful material have so far been unsuccessful. Of the various methods which have been followed to attain this goal and which after all have led to interesting results, although only in a scientific sense, the procedure used by C. Harries [226] may be followed as an example. He covered sheeted-out old rubber with chloroform, saturated the latter with hydrogen chloride, and separated the chloroform-soluble hydrochloride. By heating this with pyridine or other strong organic or inorganic bases, he obtained a sulfur-free regenerate. However, decomposition of the ozonide of the regenerate showed that a deep-seated change in the material had taken place during this regeneration. A shifting of the double bonds in the molecule had occurred, and the product obtained was not identical with rubber but only isomeric with it. Such regenerates may be actually vulcanized in sheet form, but only very unsatisfactory values are obtained in physical tests, so a practical application of the products obtained in this way appears to be out of the question. Today, it can be considered a certainty that the chemical combination of sulfur is an essential, but not the only important factor in the vulcanization of rubber. The mechanical properties of the vulcanizates are influenced much more by the molecular condition of the rubber. Therefore, inasmuch as a complete desulfurization of vulcanized rubber should lead to practical useful products, a way must first be found which makes possible the removal of sulfur in the mildest manner; i.e., without changing the constitution of the rubber hydrocarbon, and without essentially reducing the degree of aggregation. To date, however, there has not yet been discovered the catalyst, which permits the desulfurization without the use of heat, pressure and strong sulfur-removing materials. This problem, which is unquestionably of great importance with regard to the explanation of vulcanization, therefore, remains unsolved.

The reclaimed rubber used in the rubber industry to the greatest extent consists of rubber in the vulcanized condition. We are content to convert the scrap into the form so essential for the rubber industry, a plastic condition, and extract from it at this point undesired substances contained in it, as

[226] *Ber.*, **46**, 733 (1913).

well as the free sulfur. How this is accomplished, and whether only the plasticization or the removal of impurities also is desirable, depends chiefly upon the kind of scrap used. As raw material for the manufacture of reclaimed rubber, automobile tires, inner tubes, and rubber shoes, i. e., articles with and without fabric insertions, are chiefly used. Corresponding to the differences in scrap, the reclaiming processes may be divided primarily into two different groups. The first includes those processes in which fabric-free scrap only is plasticized, while the other includes those processes in which a separation of fabric or other added substances from the rubber is accomplished in addition to the plasticization of the rubber. The most important preliminary operation in both classes is a careful sorting of the scrap according to kind and quality, since the final product is largely dependent on the scrap used.

Purely plasticizing processes are employed: (1) for working up high-grade scrap which is free from fabric at the beginning, and (2) for working up scrap which has been freed from enclosed substances by the mechanical separation processes to be described later.

The plasticization takes place during the heating of the finely divided scrap in an autoclave under pressure, with or without the addition of softeners. Thus, according to the Gare process,[227] which is carried out without softeners, the rubber waste is fused together at a fairly high temperature (about 200° C.) under pressure. A homogeneous mass is produced, which may be molded directly to form rubber articles. When softeners are used, the finely divided and swollen (in the softener) scrap is heated in an autoclave under pressure. As softeners, high-boiling liquids are used; e.g., mineral, rosin or vegetable oils, which remain in the reclaimed rubber, or plasticizing agents such as turpentine, aniline, creosote, and phenol, which may if desired be recovered with steam at the end of the process. With certain scraps such as inner tubes, heat treatment under pressure is not always necessary, as Penther has pointed out. According to this process, the scrap is passed through tight, cooled mill rolls, whereby it actually falls to pieces at first, but on continued cold working reunites into sheets which, even if somewhat "dry" for the manufacture of new rubber products such as calendered sheets, are still useful. This process found a wide use and rendered good service in Germany during the World War. All such purely plasticization-process reclaimed rubbers are also designated "Präparate" in Germany.

The processes employing a separation of fabric from scrap may be divided primarily into two kinds. In one group belong those procedures by which the cellulose is destroyed through chemical agents, or is transformed into water-soluble compounds and then washed out. The second group includes all those processes in which the fibrous material is preserved. Here the rubber is separated from the fabric mechanically, or it is taken into solution and the separation carried out by filtration or some other suitable method.

The processes of the first group may be divided as follows, corresponding to the agents used for the destruction of the cellulose: (1) acid process, (2) alkali process, and (3) neutral process.

The oldest acid process is probably that of Mitchell[228] in which the ground scrap is heated in an autoclave under pressure with sulfuric or hydrochloric acid. In this way the fibrous material is destroyed, the rubber plasticized, and the free sulfur and acid-soluble pigments are removed. (Later, the scrap

[227] Ger. Pat., 235,573 (1909).
[228] U. S. Pat., 249,970, Nov. 21, 1881; 250,943, Dec. 13, 1881; 395,987, Jan. 8, 1889; Brit. Pat., 20,289 (1890).

was heated at atmospheric pressure with diluted acid or sodium bisulfate. After this treatment, the acid is thoroughly washed out with water, and the rubber material is heated with steam under high pressure. Since it is extremely difficult to wash out the last traces of acid from the reclaimed rubber, however, and the rubber is extremely sensitive to traces of acid remaining in it, this process is being abandoned generally in Europe, since the only remedy is an alkali treatment following the acid. According to K. Gottlob,[229] the process is still frequently used in America.

In the alkali process,* finely divided scrap is heated with an 8 to 10 per cent caustic soda solution at 12 to 16 atmospheres pressure in order to free the scrap from cellulose. The action is the same as in the acid process; the cellulose is broken down, the rubber is plasticized, and the free sulfur and alkali-soluble pigments are dissolved. According to F. Kirchhof,[230] the process is usually carried out as follows:

The finely divided scrap together with caustic is placed in a vessel which is equipped with double walls and a stirrer through its axis. The inner vessel is heated and agitated until the desired pressure is reached and the temperature corresponding to this pressure is then maintained by passing steam through the outside shell. After this heat treatment, the pressure is allowed to drop to 2 atmospheres, when the release valve of the inner vessel is opened and the contents are forced out. The rubber is taken to settling tanks and washing Hollanders, next to centrifuges and finally to a drying system. In order to remove bits of metal, high quality reclaimed rubber is still treated in straining machinery, which may be either a tubing machine with steel screens to retain metal while passing the reclaimed rubber or a vertical hydraulic press (with a screening arrangement). The removal of the alkali by washing is as important in this process as is the removal of acid in the acid process.

W. G. Martin [231] has shown that very small amounts of sodium hydroxide shorten the period of vulcanization considerably, while larger amounts (over 0.5 per cent) have the opposite effect; i.e., they retard vulcanization until, with an addition of 5 per cent, vulcanization would no longer take place in the mixture which was used.

In the neutral processes the finely divided scrap is treated with sodium sulfite solution,[232] with heating and with or without pressure. The free sulfur goes into solution, the fabric is destroyed, as is part of the pigment, and the rubber is plasticized.

The American process described by T. Schopper,[233] in which the scrap is treated with a solvent for cellulose, may be mentioned. The swollen cellulose is not separated from the rubber, however, but remains with it. The mass thus obtained is then reclaimed as usual and treated with steam. It is extremely doubtful whether the process which employs ammoniacal copper oxide as the solvent for cellulose, yields stable reclaimed rubber or rubber goods, in view of the notoriously detrimental effect on rubber of all copper compounds which are attacked by fatty acids. It would be difficult to remove the copper compounds from the reclaimed rubber completely. Soluble iron, copper, and

[229] "Technologie der Kautschukwaren," p. 120, Braunschweig, **1925.**

* Translator's Note. Most of the reclaimed rubber is today manufactured by the alkali process. The basic patent for this process was issued to A. H. Marks in 1899 [U. S. Pat., 635,441, October 17, 1899; Brit. Pat., 11,159 (1899)]. This patent was the first patent covering a commercial method for reclaiming rubber with alkali, and thus represents a major development in the rubber industry.

[230] "Fortschritte in der Kautschuk-Technologie," p. 144, Dresden and Leipzig, **1927.**

[231] Torrey, J. and Manders, A., "The Rubber Industry," p. 205, London, **1914.**

[232] Ger. Pat., 112,017, 112,500, 150,271.

[233] *Gummi-Zig.*, **30**, 325 (1916).

manganese compounds are well known to be oxygen carriers. They cause a rapid oxidation and therefore a premature deterioration of rubber articles (*see* p. 604).

The processes by which the fibrous material is also reclaimed may be classified in two groups: (1) Solution processes, and (2) Mechanical separation processes. The fibrous material which is obtained can often be used only for certain special purposes such as paper-board manufacture, because of its short fiber length.

The solution processes proceed in general by breaking down the vulcanized rubber in the presence of solvents under heat and pressure. The pigments and fibrous material are separated by filtration or other suitable manner, and the rubber substance is recovered from solution by distillation of the solvent or by precipitation. The process devised by P. Alexander[234] may be considered as an example of this type of reclaiming process. The scrap is heated for several hours in a closed vessel with 3 or 4 times its weight of benzine. The solution is separated from the undissolved pigments and fibrous material and is then heated in a closed vessel with strong caustic soda solution, the benzine being recovered by steam distillation. The emulsion becomes diluted with condensate from the steam. The impurities settle and are removed. A filterable emulsion remains, from which the rubber may be precipitated, just as from latex, by addition of acetic acid or other acidic substances, including gaseous reagents.

In the mechanical processes, the fabric which has been separated from the thick rubber articles by cutting, is disintegrated in either the wet or dry condition by means of special machinery. The free fibres are separated from the rubber by means of an air blast. The rubber is then plasticized by any of the processes described.

The several varieties of reclaimed rubber are differentiated by the method of preparation as follows: "Präparate," Mitchell or acid process, alkali process, and solution process reclaimed rubber. Appreciable quantities of undevulcanized rubber scrap which is merely ground fine are also available for use in compounding rubber for certain products. Aside from the fact that such scrap is suitable only for hot vulcanization, it is further limited in possible application, since it is not plasticized. Open-cured and molded rubber goods which contain much ground scrap frequently show an undesirable rough surface. In the manufacture of hard rubber goods, on the contrary, hard rubber dust produced from hard rubber scrap is the most important filler. It must first be painstakingly cleaned from sand and metal particles. Hard rubber in which the rubber hydrocarbon is nearly completely saturated with sulfur cannot be plasticized again; it is technically not reclaimable.

As was pointed out at the beginning of this section, reclaimed rubber may be used alone or with new rubber in producing new products. On mixing with sulfur and vulcanizing, it returns from the plastic to the elastic condition again. The conception which is generally held concerning the mechanism of the reclaiming process has already been reported in the section on Vulcanization (*see* p. 301).

Reclaimed rubber serves as a cheapener of rubber goods, especially in times of high rubber prices. Its use under appropriate conditions does not always constitute an impairment of the product; in fact a good reclaimed rubber is the full equivalent of raw rubber for many purposes and moreover, in

[234] Brit. Pat., 14,681 (1905); 25,735 (1906).

certain cases it offers advantages in factory handling. Under such circumstances it would be an extravagance, from the standpoint of economics, assuming the same price for reclaimed and new rubber, not to use reclaimed rubber wherever it can replace new rubber without appreciable lowering of quality and durability of the product. This conclusion is based on the fact that the reclaimed rubber is a domestic product, while new rubber must be imported. The use of reclaimed rubber also serves as a regulator of the price of rubber, since it lowers the raw rubber requirements. In this connection the statistics for the rubber requirements of America in 1925 are interesting, that being the year when the English governmental restriction plan of 1922 (Stevenson plan, *see* p. 15) which was designed to stabilize raw rubber prices, temporarily raised prices to an extremely high level. The retaliation of the American rubber industry is clearly expressed by the figures in Table 16.

TABLE 16.—*American Reclaimed Rubber Requirements.*

Requirements of:	First Quarter Tons	Second Quarter Tons	Third Quarter Tons	Fourth Quarter Tons
Reclaimed rubber	22,923	23,651	29,910	23,715
Raw rubber	87,642	95,771	91,534	78,926
Total requirements	110,564	119,422	121,444	102,641
Ratio: reclaimed rubber/raw rubber	26.25%	24.50%	32.80%	30.00%

According to P. Alexander,[235] the American requirements in the year 1927 were: raw rubber 371,000 tons, reclaimed rubber 183,500 tons, so that although raw rubber prices declined after 1925 the reclaimed rubber requirements did not.

Germany required 45,000 tons of raw rubber in 1927. The German reclaimed rubber requirements are not available but P. Alexander believes that some 4,500 tons of reclaimed rubber were used in that year. Accordingly, the ratio of reclaimed rubber to raw rubber is 10 per cent and the reclaimed rubber requirements compared with the raw rubber requirements appear to be considerably lower in Germany than in the United States.[236]

[235] *Gummi-Ztg.*, **42**, 2,796 (1928).

[236] An excellent discussion of present-day reclaiming methods, together with a bibliography on the subject of reclaimed rubber is to be found in Circular of the Bureau of Standards, No. 393, entitled "Reclaimed Rubber," by A. T. McPherson.

Chemical-Analytical Testing Methods

By E. Kindscher *

Analysis of Crude Rubber

As stated in previous chapters, the crude rubber of commerce is not a uniform chemical compound, but contains moisture, so-called "rubber resins," proteins and mineral matter, in addition to rubber hydrocarbon. The quantities of these non-rubber constituents vary with the botanical source of the rubber, the age of the plant from which it is obtained, the method of preparation, and other factors. The rubber which now dominates the market—that from the *Hevea* estates of the Middle East—is, as a consequence of the high state of development of plantation technique, so uniform in composition that chemical analyses by the user are seldom required. When it is necessary to explain the small differences in behavior among the commercial plantation rubbers, a more thorough study than that which can be made by determining the above-mentioned constituents, is generally required.

In the case of wild rubbers, varying quantities of earth, sand, wood and bark are also present. The inclusion of such materials results from lack of care in the collection of the latex and the primitive methods of preparation used by the natives. In wild rubber is also to be found crude impurities, such as large stones and pieces of metal, added presumably for the purpose of increasing weight. Since these inclusions have no value and must be completely removed before the rubber can be used in manufacture, a careful control of all deliveries of wild rubber is recommended. Accordingly, the first object of the analytical study of such rubber is concerned with the quantity of such worthless substances present. The next most important question, in the case of wild rubbers, has to do with the amount of pure rubber hydrocarbon, the valuable constituent of the crude product. The rubber hydrocarbon is usually determined by indirect analysis, there being no easily conducted direct method which yields satisfactory results. After the sample has been freed of coarse impurities, the naturally occurring non-rubber constituents are determined, and the content of rubber hydrocarbon is calculated by difference.

There is considerable variation in the technical value of the rubber hydrocarbon present in various types of wild and plantation rubber. Factors influencing this variation include the botanical source, the age of the plant, the method of preparation of the rubber, etc. Evaluation of this difference in technical value is not possible by the use of chemical methods. Instead, dependence must be placed on the determination of physical properties. Of especial interest in this connection are the mechanical properties of the vulcanized product, since they govern its applicability to various uses. Unless the rubber is to be used in the form of a cement, the tests of primary importance are those of experimental vulcanization and the mechanical testing of the vulcanizate. Furthermore, since the capacity of a manufactured product

*Translated by R. F. Dunbrook and V. N. Morris.

for withstanding aging frequently governs its usefulness, the determination of the mechanical properties after aging of the test vulcanizate is often desirable.

In summarizing, therefore, it can be said that in testing crude rubber the answers to two questions are sought: How much valuable material does it contain, and what technical value does it have?

Determination of the Loss on Washing

For the determination of the total content of moisture, water-soluble constituents and mechanically-included impurities in crude rubber, use is made of a process which is closely related to the usual methods employed in manufacturing practice. This determination gives the loss which is sustained in the commercial purification, consisting of washing followed by drying.

A good average sample of 1/2 to 1 kg. of rubber is taken for analysis. The weighed sample is rinsed with cold water and is then washed on a small washing mill or in a masticator, first with cold water, and then with water at 40° to 50° C. Samples which are especially tough, and which cannot readily be worked in the usual laboratory apparatus, are previously softened by washing from 1 to 2 hours in a suitable vessel with warm water, and are then rinsed on a sieve with warm water. In regard to the duration of the washing process, it can only be said that the rubber must be washed clean, but that any unnecessarily long treatment and warming is to be avoided, especially if a test vulcanization is to be made, and subsequent mechanical testing of the vulcanizate is to be conducted.

The crude rubber, purified in the manner described, is dried at room temperature in a place protected from direct sunlight. It is then weighed. The difference between the weight of the original sample and the weight of the air-dried and washed ("technically purified") rubber gives the quantity of impurities and moisture in the crude product. Approximate values for this so-called "washing loss" are shown in the accompanying table.

	Per cent
Hard fine Para	16-18
Plantation smoked sheets	1-1.3
Plantation pale crepe	0.5-1.0
Brown plantation crepe	4-6

In general, the apparatus used in the laboratory for determining washing loss should be so constructed that it differs from the factory apparatus used for washing only in having smaller dimensions. If the apparatus is used not only for washing, but also for the preparation of rubber mixes, it should be so constructed that it can be either heated by steam or cooled with water.

When the content of water-soluble material is high, as is the case with rubber such as the sprayed product made by evaporating latex according to the Hopkinson process (*see* p. 126), a different procedure may be desirable. In such cases, the water-soluble constituents, which may amount to as much as 8 per cent, can be weighed as such. "Sprayed latex" rubber is so uniform that a satisfactory determination can be made merely by extracting a finely divided, 10-gram sample several times with 5 times its weight of boiling water. After uniting the filtered solutions, and evaporating them in a previously dried and weighed flask, the residue is brought to constant weight in a drying oven at 90° C.

Determination of Moisture

For the determination of moisture, 2 grams of washed, air-dried rubber (or of the original rubber, in case it is clean enough so that it does not require washing) are dried to constant weight in a vacuum desiccator over sulfuric acid. The loss in weight corresponds to the moisture content. In general, it is advisable to cut the sample into fine pieces with shears in order to shorten the drying time. The desiccator, unless made of brown glass, should be protected from direct sunlight. The same sample can be used for the determination of the mineral constituents. All other determinations are carried out on the air-dried sample and are calculated to moisture-free crude rubber.

Determination of Mineral Constituents

In determining mineral constituents (ash), 2 grams of technically pure crude rubber are weighed and ashed in a porcelain crucible having a capacity of about 45 cc. The crucible is placed on an asbestos mat (provided with a hole about 15 cm. in circumference) in such a manner that the bottom of the crucible extends about 1/2 to 1 cm. below the hole. The crucible is then heated cautiously with a small Bunsen flame until the decomposition products of the rubber no longer escape from the crucible; whereupon the heating is continued on a clay triangle to constant weight. The ignition of the gaseous products, which might lead to losses, is avoided by the use of the asbestos mat.

The ash content of Para rubber and good plantation varieties varies from 0.05 to 0.5 per cent. Inferior plantation rubbers contain larger quantities of inorganic constituents (up to 1 per cent). In the case of plantation varieties which have been obtained by an evaporation process, the mineral content may amount to 1.5 per cent.

Determination of the Acetone-soluble Constituents

The acetone-soluble constituents of crude rubber are usually designated as rubber resins, although these substances are not closely related to resins in the chemical sense.

The first step in the determination of these constituents is to cut 5 grams of technically pure rubber into fine pieces with a pair of scissors. The rubber is then spread out on fabric which has previously been extracted with acetone. The fabric is next rolled up and inserted into a Soxhlet paper thimble, and, together with the latter, is placed in the central portion of a Soxhlet apparatus provided with a siphon. The extraction is carried out on a water bath, using acetone which has been freshly distilled over anhydrous potassium carbonate. The fabric prevents the individual rubber particles from sticking together during the extraction, and thus insures the completeness of the process. In general 8 to 10 hours are sufficient for the complete extraction of the resins. After this period, the acetone in the Soxhlet flask is distilled on the water bath, and the residue, together with the flask, is dried to constant weight in an oven held at a temperature not exceeding 90° C.

It is advisable not to choose a Soxhlet apparatus of too large a size. The central part of the apparatus provided with the siphon should have a diameter of about 35 mm. The extraction is conducted in such a manner that the acetone is siphoned every 6 to 8 minutes. Furthermore, it is expedient to

construct the central part of the Soxhlet apparatus of brown glass (or else to protect it in some other manner from the direct action of sunlight) so that in readily oxidizable rubbers an increase in the acetone-soluble constituents does not occur during the extraction. In Table 1, the resin contents of certain plantation and wild rubbers are presented.[1]

TABLE 1.—*Resin Content of Rubber.*

Kind of rubber	Resin content Per cent
Plantation pale crepe	1.8 - 3.0
Plantation sheets	2.5 - 3.0
Plantation smoked sheets	2.5 - 3.5
Evaporated latex	5.0 - 6.0
Hard fine Para	3.0 - 3.5
Ceara scraps	3.0 - 5.0
Cameroon balls	7.0 - 10.0
Lagos lumps	10
†Guayule	13.0 - 18.0
Jelutong (pontianak)	70 - 80

As previously explained (*see* p. 315), the so-called resins consist largely of free fatty acids. They are capable of exerting a considerable but variable (since they occur in variable proportions) influence on the various commercial rubbers, especially with respect to the behavior of the latter when being vulcanized. It is obvious, therefore, that the acid value of the acetone extract is a factor not to be neglected. Not only does it help to explain the behavior of a given crude rubber in commercial manufacture, but it may provide the information necessary for the correction of existing deficiencies. In the method of Whitby and Winn[2] for the determination of the acid value, 30 to 40 grams of rubber are first cut into small pieces and extracted with acetone for 48 hours in the extraction apparatus. The acetone is distilled from the extract, and the latter is brought to constant weight at 70° C. The residue is then taken up in warm neutral alcohol, and titrated with 0.1 *N* alcoholic potassium hydroxide, with phenolphthalein as indicator. The acid value, which is calculated from the results obtained, is the number of milligrams of potassium hydroxide required to neutralize the acid in 100 grams of rubber.

Van Rossem and Dekker, on the basis of their investigations, call attention to the fact that the acetone extract also contains volatile fatty acids, and as a consequence the acid value is dependent on the temperature at which the acetone extract is dried. They obtained the highest acid values when using rubber which had not been subjected to previous drying. In addition to these free fatty acids, there are also present fatty acid esters of high molecular weight fatty acids, as well as esters of water-soluble acids. If the acetone extract is saponified and the amount of alkali used is determined, and if the saponified solution, after acidifying, is extracted with ether, it is found that these last acids require for neutralization a smaller quantity of alkali than was used in the original saponification. According to the investigations of van Rossem and Dekker, the quantity of free fatty acids is in general larger than the quantity of esters, in the case of plantation rubber. They also state that the free acids consist, for the most part, of liquid and solid fatty acids and that in general the quantity of water-soluble acids is small. The errors introduced into the acid determination by drying the acetone extract at

[1] Luff-Schmelkes, "Die Chemie des Kautschuks," p. 35, Berlin, 1925.

† Translator's Note. This sample of Guayule was probably one from which part of the resin had already been removed. Untreated Guayule rubber contains over 20 per cent of resins.

[2] *J. Soc. Chem. Ind.*, **42**, 336T (1923).

higher temperatures are therefore not of great consequence. In addition to the acids which are extractable with acetone, there are also present in crude rubber other acids which are insoluble in acetone, and which can only be isolated by subsequent treatment with an alcoholic solution of an alkali (*see* p. 373).

Sometimes it is of interest to determine the nitrogen content of the acetone extract when information regarding the type of nitrogen-containing compounds in the crude rubber is desired. Since in most cases the quantities are very small (averaging about 0.05 per cent of the rubber) the micro-method proposed by Gerngrosz and Schäfer is used to advantage for their determination (*see* p. 369).

If the crude rubber has been obtained by evaporation (sprayed rubber, for example) and has not been washed or boiled with water, the acetone extract contains considerable quantities of water-soluble compounds.

Determination of Proteins

For the determination of the protein content of crude rubber, the method of Kjeldahl for the determination of nitrogen is generally used, and from the results the quantity of proteins is calculated.

A 2-gram sample of rubber is treated in a 500 cc. Kjeldahl flask with 20 cc. of a mixture of 3 volumes of concentrated and 2 volumes of fuming sulfuric acid, together with 0.1 gram of mercuric oxide. The flask is closed with a connecting bulb tube * and placed in an iron dish. It is heated, gently at first but more strongly later, so that the liquid finally comes to a boiling temperature. The boiling is continued until the solution becomes clear and colorless, 2 or 3 hours usually being required. The solution, which contains the nitrogen of the rubber in the form of ammonium salts, is diluted with 250 cc. of water, with cooling, and is then treated with 80 cc. of sodium hydroxide solution of specific gravity 1.35 and a quantity of sodium sulfide solution sufficient to precipitate all of the mercury present. Some zinc dust is added, and the flask is then connected to a condenser. The end of the condenser dips beneath normal sulfuric acid (10 to 20 cc.), contained in an Erlenmeyer flask having a capacity of about 300 cc. About 100 cc. of the contents of the flask are distilled, and the quantity of excess sulfuric acid in the Erlenmeyer flask is titrated with normal sodium hydroxide, using methyl orange as indicator. By running a blank, the amount of nitrogen contained in the chemicals used is determined.

The percentage of nitrogen contained in the rubber is calculated from the following equation: $x = \frac{1{,}400\,t}{a}$, in which "*a*" is the weight of the sample and "*t*" is the number of cubic centimeters of 1 *N* sulfuric acid neutralized by the ammonia. The nitrogen content thus determined is multiplied by the factor 6.25, which is obtained by assuming that the proteins present have an average nitrogen content of 15 to 18 per cent. The resulting value represents the quantity of proteins contained in the rubber.

In general, the percentage of nitrogen in Para and plantation rubbers varies between 0.45 and 0.50, of which, as previously mentioned, about one-tenth is in the form of acetone-soluble compounds. This corresponds to a protein content of 2.8 to 3.1 per cent. There are, however, wild rubbers (some of the African varieties, for example) with protein contents varying from 6 to 8 and even up to 12 per cent or more.

* Translator's Note. *See* Sy [*J. Ind. Eng. Chem.*, 4, 680 (1912)]. The Kjeldahl flask is also often used without being closed at the top.

Aside from this indirect procedure, several methods for the direct determination of the nitrogen-containing constituents of crude rubber have been developed. They are based on the fact that the rubber can be dissolved in suitable solvents, and the insoluble compounds containing nitrogen can be separated. Since in these methods the viscous nature of the rubber solution is disadvantageous, various processes have been proposed for avoiding this inconvenience. Beadle and Stevens [3] heat the rubber in phenetole or nitrobenzene, and pour the solution into a large quantity of benzene. F. Frank [4] heats the rubber with cymene, and separates the proteins by centrifuging and washing them with benzene and ether. The method of Spence and Kratz [5] consists of dissolving the rubber in a suitable solvent, lowering the viscosity of the solution by the addition of about 0.5 per cent of trichloracetic acid, and then heating sufficiently to permit filtration of the suspended proteins.

Determination of Rubber Content

The information obtained from the various determinations described above is usually sufficient to enable the rubber hydrocarbon content of the sample to be calculated. The pure rubber content is obtained by subtracting from 100 the sum total (expressed as a percentage) of all accompanying constituents.

The direct determination of the rubber hydrocarbon content of crude rubber has been the object of considerable experimental work. As desirable as it would be to have a reliable method for the direct determination, the procedures thus far proposed are so inconvenient and time-consuming, or else so beset with difficulties, that the indirect method, which ordinarily gives sufficiently satisfactory results, is to be preferred. There are, however, special cases for which the indirect method can not be used and in which it is necessary to prove the presence of rubber and determine its quantity approximately. In such cases, it is necessary to resort to one of the direct methods, the most important of which are briefly described below.

The simplest of the direct methods for the determination of the rubber hydrocarbon are those proposed by Fendler [6] and by Spence.[7] According to the process of Fendler, one gram of rubber, which has been dried over sulfuric acid (and preferably also extracted with acetone), is dissolved in petroleum ether, and the solution is made up to 100 cc. The insoluble portion is removed by filtering the solution through a glass tube filled with glass wool, and 50 cc. of the filtrate are shaken with 70 cc. of absolute alcohol. The hydrocarbon is precipitated, and is weighed after being dried. Spence proposed a similar process but used benzene as the rubber solvent. According to his procedure, the solution is made up to a known volume, and an aliquot portion of the same, after the insoluble constituents have been allowed to settle, is evaporated in an atmosphere of carbon dioxide and dried.

The processes described below are quite different, inasmuch as derivatives of the rubber hydrocarbon are used in the determination.

One method, based on the formation of the tetrabromide, was proposed by Budde.[8] A 0.1-gram sample is allowed to swell in 50 cc. of carbon tetrachloride for 24 hours. Then 50 cc. of a brominating liquid, consisting of 6 cc. of bromine and 1 gram of iodine in a liter of carbon tetrachloride, are added, and the solution is allowed to stand 6 hours. At the end of this time 50 cc. of

[3] *Analyst*, **37**, 13 (1912).
[4] See Torrey, J. and Manders, A. S., "Rubber Industry," p. 144, London, **1914**.
[5] *Kolloid-Z.*, **14**, 262 (1914).
[6] *Ber. pharm. Ges.*, **14**, 208 (1904).
[7] *Gummi-Ztg.*, **22**, 188 (1908).
[8] *Pharm.-Ztg.*, **50**, 432 (1905).

alcohol are added, the solution is again allowed to settle, and the liquid above the bromide is poured through a small filter, transfer of any bromide to the filter being avoided if possible. The residue remaining in the vessel is treated to remove excess bromine by using a glass rod with a broad flattened end and working the bromide with a mixture of 2 parts of carbon tetrachloride and 1 part of alcohol. The resulting solution is poured through the same filter as previously used. To remove the last traces of bromine, the bromide is swelled in 30 cc. of carbon disulfide, allowed to stand for 24 hours, and then precipitated from solution with 50 cc. of petroleum ether. The bromide is next transferred to the filter previously used, is washed thoroughly with alcohol and ether, and is dried in an oven at 40° C.[9] The filter paper containing the bromide is then folded together and cut into strips, and the whole is mixed in a platinum crucible with sodium potassium carbonate. The contents of the crucible are heated over a Bunsen burner until a clear melt results. The crucible must not be heated above a red heat. After cooling, the melt is taken up with water, acidified with dilute nitric acid, treated with a sufficient quantity of silver nitrate to convert to silver bromide and heated until the precipitate is well agglomerated. The precipitate is then filtered, and the weight of the silver bromide is determined in the usual manner. The rubber content of the sample can be calculated from the proportion $4\ Br : C_{10}H_{16} = a : x$, in which *"a"* denotes the quantity of bromine found.

Hope of improving this "tetrabromide" method has prompted considerable investigation. That the results obtained by this method are too high was early discovered. One source of error arises from the demonstrated fact that a substitution reaction accompanies the addition reaction, and makes the apparent bromine content of the tetrabromide too high. The extent of substitution varies with the temperature, the duration of the action of the bromine on the rubber, the concentration of the brominating liquid and other factors. Furthermore, it has been established that the proteins in the rubber can also add bromine to form compounds which are partly soluble and partly insoluble in the liquid used by Budde.

Lewis and McAdams [10] hoped to eliminate the errors entering the determination through substitution, by making use of a purely volumetric process, as follows: A weighed sample of acetone-extracted rubber is dissolved in pure carbon tetrachloride. The insoluble matter is filtered, and to the filtrate is added a measured volume of bromine in pure carbon tetrachloride, corresponding to an excess of approximately 150 per cent of that necessary for addition. After 2 to 4 hours, during which the reaction mixture is allowed to stand in the dark, potassium iodide solution is added to react with the excess bromine, and the resulting iodine is titrated by means of a standard solution of sodium thiosulfate. The hydrogen bromide produced as a result of substitution is determined in the same manner after the addition of potassium iodate. The value obtained in the second titration is subtracted from the results of the first titration, and the bromine obtained as described above is calculated to rubber. Fisher, Gray and Merling,[11] on the basis of their experience, doubt whether this method is capable of yielding exact results.

The derivatives of the rubber hydrocarbon which are produced by the action of nitrogen oxides were suggested as the basis for a possible method of

[9] The remainder of the process as described is not that proposed by Budde. His suggestion was to oxidize with concentrated nitric acid in the presence of silver nitrate, a procedure which leads to the loss of bromine.

[10] *J. Ind. Eng. Chem.*, **12**, 673 (1920).

[11] *J. Ind. Eng. Chem.*, **13**, 1031 (1921).

analysis by Harries[12] and by Alexander.[13] Harries found that by passing moist nitrogen trioxide (produced by heating nitric acid with arsenic trioxide) into a solution of rubber in moist benzene, a nitrosite of the composition $C_{10}H_{15}O_7N_3$ was formed. This compound could be filtered in a Gooch crucible, and, after purification with petroleum ether and ether, could be dried in an oven at 80° C. Alexander, on the other hand, made use of a solution of rubber in carbon tetrachloride, into which he passed an oxide of nitrogen, which was produced by heating starch with nitric acid. He obtained a product with a composition corresponding to $C_9H_{12}O_6N_2$, the formation of which he explained by assuming that, during the reaction, carbon dioxide is split off by oxidation. This splitting off of carbon dioxide was not confirmed by Wessen.[14] This latter investigator, in conjunction with Knorr, thereupon developed a method for the direct determination of rubber, according to which the nitrosite is not weighed as such, but is "burned" with potassium dichromate and sulfuric acid. Since all of the carbon of the rubber passes through the nitrosite into carbon dioxide in this process, the determination of this latter gas permits the calculation of the proportion of rubber hydrocarbon present in the original sample.

The method of Wessen and Knorr was carefully tested by Tuttle and Yurow,[15] who proposed certain modifications. According to the suggestions of these latter investigators, the acetone-extracted rubber is dissolved in chloroform, and oxides of nitrogen are passed into the solution until the green color of the solution remains permanent. The nitrous oxides are formed by the action of nitric acid (of specific gravity 1.3) on arsenic trioxide. The reaction mixture is allowed to stand over night and is then filtered through a Gooch crucible. The filtrate is evaporated to dryness. Both the residue and the contents of the Gooch crucible are dissolved in acetone. The resulting solution is filtered and weighed. After permitting any insoluble portion to settle out, an aliquot part of the liquid is evaporated to a small volume and is then transferred to a combustion boat. The solution in the boat is evaporated to dryness, and the last traces of solvent are removed by heating in the presence of a dilute solution of ammonia. The boat is then placed in a combustion furnace, and the products of combustion are passed through eight absorption vessels. The first three of these vessels contain sulfuric acid and potassium dichromate, the fourth zinc dust, the fifth and sixth soda-lime and calcium chloride, the seventh sulfuric acid and potassium dichromate and the eighth a dilute solution of palladium chloride. The increase in weight of the fifth, sixth and seventh absorption tubes gives, after combustion, the total amount of carbon dioxide formed, from which the rubber content of the sample can be calculated.

Determination of Rubber in Rubber-Bearing Plants *

D. Spence and M. L. Caldwell [*Ind. Eng. Chem., Anal. Ed.*, **5**, 371 (1933)] have made a thorough, systematic study of the possible methods for determining the rubber content of guayule shrub and other rubber-bearing plants, and have developed a quantitative method of their own. The effect of the following important factors on the accuracy of the method was studied:

"Respiration changes occurring in the plant tissue after harvesting and before analysis.

"The influence of colloidal protective materials in the plant structure upon the extraction of the rubber.

[12] *Ber.*, **35**, 3256, 4429 (1902); **36**, 1937 (1903); **38**, 87 (1905).
[13] *Z. angew. Chem.*, **18**, 164 (1905); **20**, 1355 (1907); *Gummi-Ztg.*, **21**, 727 (1908).
[14] *J. Ind. Eng. Chem.*, **6**, 459 (1914); **9**, 139 (1917).
[15] *India Rubber World*, **57**, 17 (1917).
* Translator's Note.

"The effect of the type of rubber solvent used.
"The oxidation which occurs during the drying of films of extracted rubber."

The effect of respiration changes was prevented by desiccation to less than 9 per cent moisture or by storage of the freshly ground material in tightly packed and stoppered jars.

The removal of colloidal protective materials was accomplished by boiling for 3 hours with 1 per cent sulfuric acid followed by a further treatment with steam in an autoclave for 3 hours.

Benzene was found to be the most suitable rubber solvent, and the oxidation of the rubber film during drying was prevented by the addition of an antioxidant to the rubber solution.

A detailed description of the method follows:

Preparation of Sample.. "The plants to be analyzed, washed free of adhering soil, are first coarsely crushed by two passes through corrugated differential laboratory mill rolls set up as tightly as possible. This material is then ground successively with a Universal grinder and a corn mill. (Made by Landers, Frary, and Clark, New Britain, Conn. The use of an attrition-type mill operated with a reciprocating motion for the finer stages of grinding has proved effective in preventing the agglomeration of the rubber in guayule shrub.) After each stage of grinding, the shrub is thoroughly mixed and quartered by means of Jones ore samplers of various sizes. The final quarter is divided into two lots of a little more than 5 grams each and one lot of approximately 10 grams. The remaining shrub is preserved, packed tightly in an airtight glass jar, for use in case of emergency.

"Duplicate 5-gram samples are then weighed out on the analytical balance from the [illegible] samples divided out with the sampler. These are transferred to Coors porcelain extraction thimbles, which for convenience are 22 mm. in diameter by 70 mm. high, inside measurements, with 2-mm. perforations in the bottom. A thin layer of wool batting is placed below and above the shrub to prevent loss.

"The moisture content of the sample is determined at the same time by vacuum-drying the 10-gram sample at 110° C. in a Petri dish.

Removal of Water-Solubles. "The samples in the porcelain thimbles are boiled in a 1 per cent solution of sulfuric acid for 3 hours. For this operation it has been found convenient to use a monel metal bath provided with a water-sealed lid and water-cooled condenser outlet to maintain the acid concentration. A punched plate is employed to hold the thimbles upright on a monel metal screen. After 3 hours the samples, still saturated with acid, are transferred, along with the supporting tray, to an autoclave where they are steamed for 3 hours at 30 pounds per sq. in. (2.1 kg. per sq. cm.) pressure.

"For the subsequent operation of leaching to remove the materials rendered water-soluble by the preceding treatments, a copper bath has been found convenient in which the thimbles are held upright by holes in the lid and are supported on a wire screen 4 cm. from the bottom. Water at 60° C. from a storage-type electric water heater is run through each thimble individually in a slow stream. Three hours of leaching are sufficient completely to remove all water-soluble materials. The amount of material thus removed can be determined quantitatively with fair accuracy, by difference, by weighing the thimbles before and after the completed analysis.

Acetone Extraction. "After water-leaching, the thimbles are immediately placed in siphon cups of the Underwriters' Laboratories type and are extracted for 12 hours (on an electric hot plate) using about 150 cc. of acetone. If the water-solubles are to be determined, as above, this extraction must, of course, be made in a tared flask.

Extraction of Rubber. "The acetone left in the sample from the preceding operation is first removed by heating the thimbles in the vacuum oven for about half an hour. The rubber is then extracted with 150 cc. of benzene in the usual way. At least 16 hours are required for this operation.

Drying of Rubber. "The benzene extract of the shrub is evaporated, dried, and weighed in the same tared flask used for the extraction. Before evaporation 5 cc. of a 0.1 per cent solution of dimethyl-*p*-phenylenediamine in benzene is pipetted into the rubber solution. A correction, based upon a blank determination, is made for this material in calculation of the results. The rubber solution is evaporated on a water bath and then dried to constant weight in a Freas oven at 105° C. Overnight drying has been found very convenient for this last step. The flask is finally weighed to three decimal figures. Accuracy to three significant figures in the final result expressed as a percentage of the dry weight of the sample has been found sufficient for all purposes."

Determination of Balata in the Presence of Rubber

It is known that the balata hydrocarbon can be separated from resins and impurities by dissolving the crude product in petroleum ether with the aid of heat, and cooling the solution to — 16° C. In this manner the balata hydrocarbon separates as a white precipitate, while the resins, for the greater part, remain in solution, and the solid impurities remain in suspension. On this fact, C. Charleson[16] bases a process for the separation of the two hydrocarbons in a balata-rubber mixture, such as is used in the manufacture of golf balls. According to his method, the sample is milled into the form of a thin sheet, or else is cut into fine pieces, and 2 to 3 grams are weighed. The weighed sample is then dissolved in a 250 cc. flask with a wide neck by frequent shaking on a water bath, using as solvent 150 cc. of light benzine (boiling under 115° C.). The solution is cooled first to room temperature and then, by means of a cooling mixture, to at least — 12° C. The rubber remains in solution, while the balata hydrocarbon, mixed with inorganic constituents which may be present as impurities, is precipitated. The solution is filtered through a cold filter with suction, and the residue is washed about four times, using 25 cc. of cold benzine each time. Before weighing, the precipitate is dried on a watch glass at a temperature of 60° to 65° C. Inorganic substances, which may be present in the balata hydrocarbon, must then be determined by ashing, or by dissolving the balata and filtering or centrifuging the solution.

Analysis of Rubber Solutions

The investigator of rubber cements or solutions is concerned in general with the type and quantity of the solvent and of the inorganic constituents, as well as with the content of rubber and other organic substances.

For the determination of the type of solvent, a sample of the material to be investigated is subjected to steam distillation. The distillate is then placed in a separatory funnel, and separated from water which has been carried over. It is then dried with calcium chloride or in some other manner, and fractionated or analyzed according to the known methods for solvent analysis.[17]

For the determination of the quantity of solvent, a weighed sample of the rubber solution is transferred to a weighing glass with a broad base, and is then evaporated and dried in a vacuum. The difference in weight gives the content of the solvent.

The dry residue is then removed from the weighing glass, cut into small pieces, and extracted in acetone as previously described (*see* p. 349). According to the method of Morawski, the acetone-soluble portions are then dissolved in acetic anhydride and are tested with concentrated sulfuric acid for the presence of colophony. If this material is present there appears a violet color, which does not persist very long. A quantitative determination of colophony can be made according to the method of Wolff-Scholze. (*See* p. 366.)

In determining the kind and quantity of inorganic fillers, a weighed sample of the rubber solution is diluted with a suitable solvent, such as petroleum ether or ether. The inorganic substances are then separated by filtration or

[16] *India Rubber World*, **72**, 410 (1925).

[17] *Cf.* Holde, B. D., "Kohlenwasserstofföle und Fette," 6th ed., Berlin, **1924**.

centrifuging and are washed, dried and weighed. Further identification can then be made according to the analytical procedure given for vulcanized rubber (*see* p. 384).

Investigation of Unvulcanized Rubber Compounds

The investigation of unvulcanized rubber compounds follows the methods described for the chemical testing of vulcanized rubber (*see* below). It is to be observed, however, that mixtures which contain bitumen or tar products must first be vulcanized, since otherwise the process fails. For an approximate separation of mixtures which contain asphalt and unvulcanized rubber, the method of J. Marcusson can be used. The mixture is dissolved in benzene, and the solution spread over kieselguhr contained in a Soxhlet paper thimble. After removal of the benzene by drying, the kieselguhr is extracted with low-boiling benzine in the extraction apparatus of Gräfe. The rubber goes into solution along with the mineral oil coming from the asphalt, but the asphaltic substances remain on the kieselguhr. The latter can then be extracted with chloroform and can be weighed after evaporation of the solvent. Separation of the mineral oil from the rubber can be obtained by acetone extraction after evaporation of the benzene solution.

Determination of the Botanical Source of Crude Rubber

The investigation of the acetone-soluble constituents in a sample of crude rubber can yield certain information regarding the botanical source of the rubber. As was shown by Hinrichsen and Marcusson,[18] the types of rubber obtained from the various species of *Hevea* may be differentiated from most other types by the fact that the acetone-soluble constituents of the former exhibit no optical activity. For determining the optical activity, the acetone extract is taken up in pure benzene, and the solution is tested by means of a polarimeter. The absence of optical rotation indicates Hevea rubber. If the solution is so dark that the field of view of the apparatus is darkened too much, it may be diluted further with benzene, or treated with Fuller's earth, and the filtered solution tested. If the rotation is too small to be determined with exactness, the unsaponifiable portion of the acetone extract, which contains the optically active material, is isolated (*see* p. 364) and tested according to the method described above.

Analysis of Vulcanized Rubber

In view of the unusual methods which are used in preparing rubber compounds and vulcanized rubber goods, complete uniformity of chemical composition is not to be expected. The preparation of a representative sample of the material to be analyzed is therefore the first and most important problem; and the success of the analysis will depend largely upon the care used in sampling and the judgment exercised in the choice of the sample.

Sampling

Before selecting the sample, it is necessary to determine whether the surface of the rubber contains substances which are foreign to the rubber and have accidentally found their way there, or whether substances

[18] *Z. angew. Chem.*, **23**, 49 (1910); **24**, 725 (1911).

are present which have been added for the purpose of preserving or decorating the commercial rubber product. Impurities, lacquer or varnish layers, etc., must be very carefully removed by mechanical means. Loosely held powdered materials, such as talc, china clay, starch, etc., are easily removed by tapping the surface gently or carefully dusting it with a soft hair brush. On the other hand, materials which have bloomed out on the surface, such as sulfur and paraffin hydrocarbons, as well as oils and waxes which obviously came from the rubber compound, are part of the rubber sample.

In the case of products such as rubber-insulated electrical conductors, all coverings of cloth, wire, or tape, as well as the metal inclosed, must be removed. With such products as hose (or other laminated material), the rubber layer is separated from the fabric (provided the rubber is thick enough); and in case various rubber compounds are involved, they are treated separately. In such cases it must also be remembered that, if necessary, the rubber in the fabric can also be examined for quality and quantity. The same is true of articles which are usually built up of various rubber compounds; pneumatic tires and rubber footwear, for example.

The average sample is taken from the rubber material prepared in the above manner. In the case of soft rubber goods, the sample is cut with scissors into such small pieces that it all passes a 40-mesh sieve (40 meshes per square cm.; open area within each mesh 1.4 sq. mm.) with shaking and leaves no residue. "It-Platten" (asbestos packing)[19] is pulled apart by hand as much as possible. Rubber-coated substances, in which the rubber cannot be separated from the fabric,[20] are cut with scissors into small pieces about 1.5 sq. mm. Hard rubber samples are prepared by rasping with a coarse file, and the powder is freed from any iron particles with a magnet. Unvulcanized rubber compounds and reclaimed rubber are cut with scissors or are rapidly milled into a thin sheet at the lowest possible temperature.

After the reduction to small pieces, the average sample is thoroughly mixed and is then preserved in a glass-stoppered flask, which is kept in a cool place protected from light.

Moisture

One to two grams of the average sample (prepared as described above) are dried to constant weight on a watch glass in a vacuum desiccator over concentrated sulfuric acid or phosphorus pentoxide. The loss in weight, based on the weight of the original sample, is called moisture.

The use of higher drying temperatures than room temperature is only advisable if it is known with certainty that the rubber compound contains no substances which are volatile under these conditions. In such cases, the determination is carried out at about 80° C. without the use of a vacuum.

The results of the procedures discussed below are all expressed in terms of percentages of the weight of the dry rubber present. The determinations, however, are carried out on the original sample and not on the dried sample.

[19] Hauser, E. A., "Latex" (English translation by W. J. Kelly), p. 139, Chemical Catalog Co., Inc., 1930.

[20] Sometimes a separation can be effected after swelling in benzene.

Water-soluble Substances

By treating the rubber sample with warm water, the following substances are partially or entirely dissolved: starch, gelatin, glue, glycerol and certain accelerators of vulcanization. An alkaline reaction of the aqueous extract is frequently due to the treatment of the rubber goods with alkalies.

The following substances can be detected qualitatively in the aqueous extract:

Starch, by the appearance of an intensive blue color on the addition of iodine solution.

Glue and gelatin, by the formation of a flaky precipitate on the addition of an aqueous solution of tannic acid. The presence of nitrogen is confirmed by mixing the filtered and dried precipitate with finely pulverized soda lime and heating the dry mixture in a small ignition tube. In the presence of glue or gelatin, ammonia vapors, which are detected by their odor or by means of red litmus paper, are evolved.

Aniline, by the appearance of a bluish-violet color on the addition of a solution of bleaching powder. The color soon changes shade.

Alkalies, by titration with 0.1*N* sulfuric acid, using phenolphthalein as indicator.

Glycerol, by rapidly heating the dry residue from the aqueous extract with double the quantity of potassium bisulfate. In the presence of glycerol, a strong odor of acrolein is evolved.

To obtain an approximate idea of the quantity of water-soluble constituents contained in the rubber sample, one proceeds as follows: At least 10 grams of an average sample are boiled for 10 minute periods with the 5-fold quantity of water until no more water-soluble substances are extracted from the rubber. In general, three extractions are sufficient. The combined filtrates are evaporated in a dried and weighed porcelain dish, and the residue is dried to constant weight at 100° C.

Acetone-soluble Constituents

Acetone completely dissolves the following substances from rubber compounds: the so-called "rubber resins," as well as resins and resin oils which were added to the rubber, mineral oils, paraffins, waxes, lanolin, cellulose ethers and cellulose esters, naphthalene, aniline, vulcanization accelerators and their decomposition products, certain organic dyes and antioxidants, and the sulfur which is not chemically combined ("free sulfur").

In addition, acetone partially dissolves the following materials from rubber compounds: fatty oils, oxidized fatty oils, sulfurized fatty oils and those treated with sulfur chloride (factice), as well as tarry and asphaltic constituents.

The duration and completeness of the acetone extraction depends not only on the kind of rubber sample and its degree of subdivision but also on the rate of extraction and the choice of a suitable extraction apparatus. Among the common types, the Soxhlet apparatus (Fig. 53) is most suitable, if the dimensions are adapted to the size of the sample to be tested. Since 5 grams of the rubber sample are usually taken for extraction, the central part *A* of the apparatus, which is provided with the syphon, should have a diameter of approximately 35 mm., and the flask *B* should

have a capacity of not more than 200 cc. The extraction is carried out on a water bath or an electrically heated hot plate. The operation is so regulated that the acetone is siphoned off every 6 to 8 minutes from part *A*. The extraction is considered complete when the solvent no longer removes any of the constituents from the rubber compound.

The extraction can be accomplished in a shorter time if the "standard apparatus," which has been prescribed by the Verein Deutscher Elektrotechniker for the extraction of the rubber from high tension rubber-insulated conductors, is used. The dimensions of this apparatus have been specified accurately.[21] (Figs. 54 and 55.) It consists of a flask *A*

Figure 53 (left)—Soxhlet apparatus.

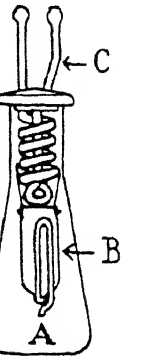
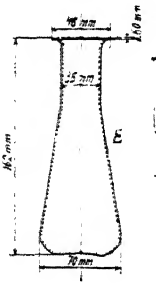
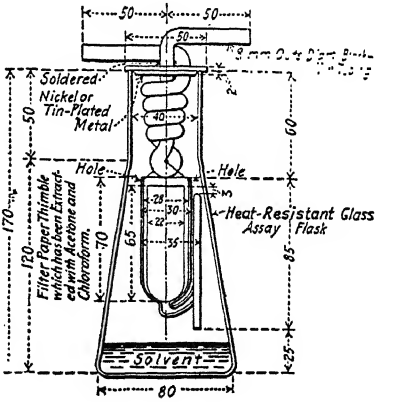


Figure 54 (right)—Standard extraction apparatus.

Figure 55 (lower left)—Individual parts of the standard extraction apparatus.

Figure 55a (lower right)—A. S. T. M. standard extraction apparatus. (All dimensions in millimeters.)





made of Jena glass, the glass vessel *B* provided with a siphon, and the suspended condenser *C*, which is made of copper tubing heavily coated with tin. By means of two adjustable metal hooks soldered to the condenser, the siphon cup, which is provided with two small holes, can be suspended beneath the condenser. This apparatus possesses the advantage of extracting the rubber at the boiling temperature of the acetone. After the removal of the siphon cup, it can be used for other purposes, e.g., heating under a reflux condenser.*

The determination of the acetone-soluble content of rubber is carried out in the following manner: Five grams of the sample, after having been reduced to small pieces, are wrapped in a linen or muslin cloth previously extracted with acetone and chloroform (or are inserted in a paper thimble) and are then placed in the siphon cup of the "standard apparatus." The latter is attached to the metal hooks on the condenser. To the previously dried and weighed flask provided with chips to prevent bumping are added about 50 cc. of acetone (freshly distilled over dehydrated potassium carbonate), and the condenser, together with the siphon cup, is inserted. The extraction is carried out on a water bath or on an electrically heated hot plate. The heating is so regulated that the siphon cup is emptied every 2½ to 3½ minutes. In the case of soft rubber goods, the extraction is in general completed within 8 hours. Otherwise, it is continued for an additional 4 hours or longer. In the case of hard rubber goods, the extraction must frequently be continued for a period of 48 hours. After the extraction, if convenient, the apparatus is allowed to stand over night, for by so doing it may be possible the next day to draw conclusions about the presence of certain organic accelerators from the crystalline material which has separated. The solvent is then evaporated on a water bath at the lowest possible temperature. The flask, together with the residue, is dried to constant weight in an oven at a temperature of about 70° C. The use of a vacuum drying oven is only advisable if it is known with certainty that the acetone extract does not contain substances which are volatile under these conditions.

In many cases it is advisable to check the value obtained in the determination by weighing the extracted rubber sample. In doing this, however, it must be taken into account that the extracted material is susceptible to oxidation to a high degree. For this reason, the sample is protected from light, and is dried *in vacuo* at room temperature, or in a stream of nitrogen at the lowest feasible temperature. If the analysis of the extracted sample is not continued immediately, it is preserved in a glass-stoppered flask which is protected from light and stored in a cool place. This procedure is necessary to prevent the oxidation of the extracted sample.

According to recent studies, soaps are formed during vulcanization by the reaction of the basic pigments added to the rubber with the naturally occurring acids in the rubber or with the organic acids which have been intentionally added. If in the course of the analysis basic pigments have been detected, the acetone extraction is followed by an extraction with a solvent for soaps, such as benzene-alcohol (8:2) or chloroform-alcohol (8:2). The presence of metals in the extract shows that soaps were present in the sample.

In order to carry out the determinations of the individual constituents of the acetone extract (as described below), 4 to 5 grams of the rubber sample must ordinarily be used for the acetone extraction.

Sulfur in the Acetone Extract

The dried acetone extract is treated with one gram of magnesium oxide and some nitric acid-bromine mixture,[22] and is heated first on the

[22] The nitric acid-bromine mixture is prepared by shaking 90 grams of nitric acid of sp. gr. 1.48 with 10 grams of sulfur-free bromine and allowing the mixture to stand for some time.

water bath and finally on the sand bath to oxidize the sulfur completely. The contents of the flask are then transferred to a porcelain dish, the flask being washed out with hot water. After evaporation to dryness on the water bath, the residue is treated three successive times with 5 cc. portions of concentrated hydrochloric acid (evaporating to a fuming condition each time). The mass is then taken up with 5 cc. of concentrated hydrochloric acid and the solution is transferred to a beaker (washing out the container previously used with hot water).

The volume of the solution is brought to about 100 cc. and the sulfate is precipitated with hot 0.1*N* barium chloride solution at the boiling temperature. After standing over night, the barium sulfate is separated by filtration and washed free from chlorine with hot water. After ashing the filter paper in a porcelain crucible, the barium sulfate is brought to constant weight at red heat.

The acetone extract may contain organic sulfur compounds, in which case the possibility exists that the sulfur may not be entirely precipitated by the barium chloride (on account of the formation of sulfonic acids). The method is then modified as follows: The acetone extract is oxidized with the nitric acid-bromine mixture in the presence of magnesium oxide. The contents of the flask, after boiling on the sand bath, are not transferred to a porcelain dish, but to a 200 cc. round-bottomed Pyrex flask, and are treated according to the method of J. Rothe for the determination of the total sulfur in rubber mixtures (*see* p. 376).

In such cases the following procedure [23] can also be used to advantage: Fifteen to twenty cc. of nitric acid of specific gravity 1.40 and one drop of sulfur-free bromine are added to the acetone extract. After standing for a short time, the extraction flask is covered with a watch glass containing a hole and is placed on a cold water bath and slowly warmed. After heating for one hour, the violent reaction has subsided. The mixture, while still hot, is transferred to a porcelain evaporating dish, which is unglazed on the outside and about 5 cm. in diameter. The flask is rinsed with concentrated nitric acid which is then added to the evaporating dish. The contents of the evaporating dish are next evaporated on the water bath until they fume. Evaporation to fumes with 3 cc. portions of concentrated nitric acid is repeated twice. The residue, which has been evaporated to a thick syrupy consistency, is dissolved in several drops of ethyl alcohol, and is stirred and warmed with a finely pulverized mixture of sodium carbonate and sodium nitrate (5:3) to a uniform paste, which is then covered by sprinkling a sufficient quantity of the salt mixture over the top. This procedure is followed by careful drying at 120° to 130° C. The evaporating dish is then covered with a similar inverted dish, and the contents of the flask are brought to fusion by carefully heating. The time of fusion, which toward the end can be accelerated by removing the cover dish and shaking the evaporating dish (which is held with crucible tongs) amounts to 1½ to 2½ hours. Before the fused mass has entirely cooled, it is dissolved in boiling water. The solution, acidified with hydrochloric acid, is evaporated to dryness. The residue is heated for 2 hours in a drying oven at 135° C. and, after moistening with concentrated hydrochloric acid, is taken up with water. The solution is filtered, and the sulfate in the filtrate is precipitated at

[23] Lunge-Berl, "Chemisch-technische Untersuchungsmethoden," 7th ed., Vol. 3, p. 1220, Springer, 1921-4.

boiling temperature with a hot 0.1*N* barium chloride solution. The barium sulfate is treated in the manner previously described.

As previously indicated, the above two procedures give not only the quantity of free sulfur, but also the sulfur contained in the acetone extract in the form of organic compounds. For the determination of "the true free sulfur," W. J. Kelly [24] devised the following procedure:

The acetone extract is treated with 50 cc. of a cold saturated solution of sulfur in 95 per cent ethyl alcohol, and the total weight is determined with an accuracy of 0.5 gram. The mixture is then warmed to about 50° C. for a few minutes and slowly cooled. Any losses, which are determined by weighing, are replaced by adding pure 95 per cent alcohol. The flask is stoppered and is allowed to stand for about 24 hours. The solution is then carefully decanted. The residue is washed two or three times by decantation with 5 cc. of the saturated solution of sulfur in alcohol, and is dried at 100° C. for one-half hour. The remaining "true free sulfur" can then be determined as barium sulfate directly or after oxidation with nitric acid-bromine mixture in the presence of magnesium oxide. The difference between the acetone-soluble and the true free sulfur is the amount of sulfur combined with the organic compounds. The process is obviously only applicable when the acetone extract contains no organic compounds which are insoluble in 95 per cent alcohol or which contain sulfur.

The volumetric determination * of the free sulfur in rubber has recently received considerable attention. A number of procedures have been proposed. W. D. Guppy [*Trans. Inst. Rubber Ind.*, **7**, 81 (1931); **9**, 59 (1933); *India Rubber J.*, *Tech.*, **5**, 360 (1932); **6**, 512 (1933)] has described a method based on the reduction of the free sulfur in vulcanized rubber (not the acetone extract) by means of tin. The hydrogen sulfide formed in the reduction is absorbed in a solution of cadmium acetate. The resulting cadmium sulfide is then treated with a standard iodine solution and the excess of iodine is determined with sodium thiosulfate solution. The amount of free sulfur is calculated from the volume of iodine solution used in the oxidation.

A. Castiglioni [*Z. anal. Chem.*, **91**, 32 (1932); *Rubber Chem. Tech.*, **6**, 412 (1933)] bases his method for the determination of free sulfur on the formation of potassium thiocyanate when the acetone extract of rubber is boiled with potassium cyanide. The excess KCN is decomposed with formaldehyde and the thiocyanate is determined volumetrically with standard silver nitrate. The procedure is as follows:

"Boil the acetone extract for 0.5 hour with an excess of potassium cyanide in a round flask with a reflux condenser, and evaporate the solvent on a water bath. Dissolve the dried residue in about 100 cc. of water, place it in a 200-cc. flask, add 10 cc. of 20 per cent formaldehyde solution, and agitate carefully. Acidify with 5 cc. of 30 per cent nitric acid and fill to the mark with water. Remove individual portions of 20 cc. of the liquid, and add 5 to 6 drops of 10 per cent iron nitrate solution, whereupon the liquid turns an intense blood-red color. Upon titration with a 0.05 normal silver nitrate solution a white precipitate of silver thiocyanate is formed, and the red color becomes weaker until it disappears completely, while in many cases it changes to a light bluish color. Since silver thiocyanate tends to agglomerate into cheesy masses which may contain some of the liquid to be analyzed so that the latter cannot be acted upon by the silver nitrate, the silver nitrate must be dropped slowly from the burette and the liquid must be kept in agitation during the titration. The various samples of the liquid make it possible to determine the number of cubic centimeters of silver nitrate solution required for complete precipitation of the silver thiocyanate which is present. This value multi-

plied by $\left(10 \times \frac{S}{AgNO_3}\right) = 1.8877$ and by the factor of the solution gives the sulfur content of the acetone extract which is analyzed."

[24] *J. Ind. Eng. Chem.*, **12**, 875 (1920); **14**, 196 (1922).

* Translator's Note.

The method of J. Robertson and J. Young [*J. Soc. Chem. Ind.*, **52**, 296 T (1933); *Rubber Chem. Tech.*, **6**, 518 (1933)] is based on the volumetric determination of sulfate by sodium rhodizonate.

Separation of the Saponifiable and Unsaponifiable Substances Contained in the Acetone Extract

The dried acetone extract is boiled under a reflux condenser with 25 cc. of a solution of potassium hydroxide[25] for 2 hours. The liquid is then transferred to a separatory funnel, and the flask is rinsed with an equal volume of hot water in three or four portions. After cooling, the extraction flask is washed several times with petroleum ether, which is then used to extract the alkaline solution in the separatory funnel. The extraction with fresh petroleum ether is continued as long as this solvent continues to extract portions from the watery liquid. The petroleum ether extracts are united in a second separatory funnel and are washed repeatedly with water until an alkaline reaction is no longer obtained. The petroleum ether extract is transferred to a weighed Erlenmeyer flask which is provided with porous stones to prevent bumping, the petroleum ether is evaporated, and the residue, which now contains the *unsaponifiable substances of the acetone extract,* is dried to constant weight in an oven at 100° C.

The alkaline aqueous solution which remains after the extraction with petroleum ether is acidified in the separatory funnel with dilute sulfuric acid and exhaustively extracted with ether. The ether extracts are collected in another separatory funnel, are washed with water until free from acid, and are transferred to a dry weighed Erlenmeyer flask containing "boiling" stones. The ether is evaporated, and the residue is dried in an oven at 70° C. to constant weight. The residue contains the *saponifiable substances of the acetone extract,* such as resins and fatty acids.

If the acidified aqueous solution from which the saponifiable matter has been removed is very turbid, it can be surmised that the rubber sample contained *cellulose derivatives.* In this case, the liquid is neutralized with ammonia and evaporated almost to dryness. The residue is treated with 10 cc. of copper oxide-ammonia ("Kuoxam")[26] and is allowed to stand 12 hours in a covered vessel with frequent shaking. After the addition of hydrochloric acid to the filtrate, the cellulose is precipitated with dilute sulfuric acid, filtered, dried and weighed. Obviously, in working with Kuoxam, no cellulose filters may be used.

Separation of the Constituents in the Unsaponifiable Portion of the Acetone Extract

The unsaponifiable portion of the acetone extract, separated according to the procedure just described, may contain the following: unsaponifiable acetone-soluble components of the crude rubber, mineral oils, paraffin hydrocarbons, tar and asphaltic constituents, and wax alcohols. They are separated in the following manner:

[25] The potassium hydroxide solution is prepared by dissolving 30 grams of pure potassium hydroxide in an equal quantity of water, cooling the solution, and diluting to 1,000 cc. with absolute alcohol.

[26] The "Kuoxam" is prepared by dissolving 50 grams of copper sulfate in 300 cc. of water, and adding ammonia dropwise until all of the copper hydroxide has precipitated. The precipitate is freed as completely as possible from the solution on a suction filter. The precipitate is transferred to a glass vessel, which is kept cold, and is then treated with sufficient 25 per cent ammonia solution to dissolve it completely. The "Kuoxam" must be preserved in the dark and is only stable for about three weeks.

The extract is exhaustively extracted with hot absolute alcohol. Any remaining residue contains tar and asphaltic constituents, as well as any decomposed rubber substance. (*See* p. 373.)

The alcoholic solution is evaporated on a water bath to 50 cc., and after cooling is preserved for 1 hour in an ice-salt mixture,[27] at a temperature not above —5° C. The solid substances which have been precipitated are filtered through a cold funnel (Fig. 56) and are washed with 100 cc. of 90 per cent alcohol,[28] cooled to the same temperature. The residue remaining on the filter is transferred to a dry weighed flask by pouring over it some absolute alcohol, followed by hot chloroform. The solvent mixture is then evaporated and the contents of the flask are dried to constant weight. The constituents of the acetone extract thus separated represent the *solid paraffin hydrocarbons*. However, if waxes were present

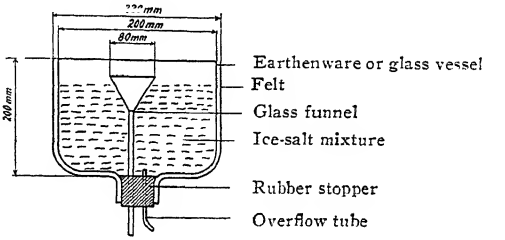


Figure 56—Ice funnel.

in the original rubber compound, the paraffin hydrocarbons then contain the alcohols of the wax. These alcohols can be separated approximately from the hydrocarbons by acetylation or in the following manner: The mixture of the above substances is heated with several drops of concentrated sulfuric acid to 150° C. (not over 180° C.). The reaction product is then mixed with calcium oxide and freshly ignited animal charcoal, and the resulting mass is extracted in an extraction apparatus with petroleum ether. After evaporation of the solvent, the solid paraffin hydrocarbons are dried and weighed.

The alcoholic filtrate, after the determination of the paraffin hydrocarbons by the "freezing method," is evaporated to dryness on the water bath. The residue is taken up with 15 cc. of carbon tetrachloride, transferred quantitatively to a separatory funnel with small portions of carbon tetrachloride (using a total of about 10 cc.), and shaken with 15 cc. portions of concentrated sulfuric acid until the acid is no longer colored. After drawing off the acid from the last extraction, ether is added to the carbon tetrachloride-water solution until the carbon tetrachloride-ether mixture forms a layer above the water (about 100 cc.). This is followed by an extraction with water, colored with methyl orange, until the wash water no longer shows an acid reaction. The carbon tetrachloride solution is then transferred to a dry, weighed Erlenmeyer flask provided with "boiling" stones, and is evaporated on the water bath. The residue is dried at 100° C. to constant weight. It then contains the liquid paraffin hydrocarbons; that is, the liquid portions of the solid paraffins which were added to the rubber compound, as well as mineral oils which were used as such or which were derived from asphaltic substances or from certain grades of factice.

[27] 2 kilograms of ice plus 1 kilogram of table salt.

[28] 90 cc. of absolute alcohol plus 10 cc. of water.

Separation of the Constituents of the Saponifiable Portion of the Acetone Extract

The saponifiable portions contain the fatty acids and the resin acids. The determination of the resin acids can be carried out by the conventional method of the Union of Soap Manufacturers of Germany.[28] For this purpose 2 to 3 grams of the resin acid-fatty acid mixture are necessary. This quantity is obtained by the appropriate treatment of a large amount of the rubber sample. The 2 to 3 grams thus obtained are accurately weighed into a glass-stoppered flask of about 150 cc. capacity and are then treated with 20 to 30 grams of absolute alcohol. The flask is immersed in cold water, and a stream of dry hydrogen chloride is passed through the liquid until no more absorption takes place. This process usually requires about three-quarters of an hour. The flask is then removed from the cooling water. After rinsing the delivery tube with a small quantity of absolute alcohol, the flask is stoppered and set aside for at least one hour. The contents of the flask are then diluted with 5 times their volume of water, and heated until the solution has become clear. The analysis is finished by gravimetric methods.

The contents of the flask are transferred to a separatory funnel and vigorously shaken with 75 cc. of ether, which also serves for rinsing out the flask. The aqueous solution is then drawn off, and the ether solution, which contains the resin acids and the ethyl esters of the fatty acids, is washed with water until the washings no longer give an acid reaction toward litmus paper. After the addition of 50 cc. of alcohol, the solution is titrated with 0.5*N* alcoholic potassium hydroxide solution, using phenolphthalein as indicator. In this operation, only the resin acids unite with the alkali to form resin soaps, while the ethyl esters of the fatty acids remain almost unchanged. One cc. of 0.5*N* potassium hydroxide solution corresponds to 0.175 gram of resin acids.

If for any reason the further investigation of the resin acids seems desirable, the process of Wolff-Scholze, in which the resin acids are determined gravimetrically, may be used to advantage. According to this method, 2 to 5 grams of the resin acid-fatty acid mixture, dissolved in 10 to 20 cc. of methanol, are boiled under a reflux condenser for 2 minutes with 5 to 10 cc. of a mixture composed of 1 volume of concentrated sulfuric acid and 4 volumes of methanol. After the mixture has been diluted with 5 to 10 times its volume of a 10 per cent salt solution, it is extracted with ether. The aqueous layer is then drawn off and extracted two or three times more with ether. The combined ether solutions are washed with the 10 per cent salt solution until neutral toward methyl orange, and, after the addition of some alcohol, are made neutral toward phenolphthalein with 0.5*N* alcoholic potassium hydroxide. One to two additional cc. of alcoholic potassium hydroxide are then added, and the ether solution is washed several times with water. The soap solution, together with the wash water, is evaporated to a small volume. By acidifying the condensed solution with dilute mineral acid and adding an equal volume of concentrated salt solution, the resin acids, including the unesterified fatty acids, may be separated and extracted with ether as above.

[28] See "Einheitsmethoden zur Untersuchung von Fetten, Ölen, Seifen und Glycerin," p. 58, Berlin, 1910.

The ether extract is dried with anhydrous sodium sulfate and filtered. The ether is evaporated from the filtrate, and the cooled residue is dissolved in 10 cc. of methanol and esterified with 5 cc. of a mixture composed of 1 volume of concentrated sulfuric acid and 4 volumes of methanol, as described above. The mixture is treated with 7 to 10 times its quantity of 10 per cent salt solution, and extracted two or three times with ether. The ether extract is neutralized with alcoholic potassium hydroxide and extracted several times with a very dilute solution of alkali. From the united aqueous and alcoholic extracts, the resin acids are extracted with ether as described above. The ether is evaporated, and the residue is dried to constant weight.

Another method for the determination of resin acids (colophony), in addition to fatty acids, was worked out by E. J. Parry.[30] According to this method, the mixture of resin acids is dissolved in 20 cc. of 95 per cent alcohol. A drop of phenolphthalein indicator solution is added and then concentrated sodium hydroxide solution (1 part sodium hydroxide to 2 parts of water) until the mixture is slightly alkaline. The solution is heated for several minutes, cooled, and transferred to a 100 cc. graduated cylinder provided with a stopper. The cylinder is filled to the 100 cc. mark with ether, 2 grams of pulverized silver nitrate are added, and the mixture is vigorously shaken for 15 minutes in order to convert the acids to their silver salts. After the insoluble silver salts have settled, 50 cc. of the clear solution, which contains the silver salts of the resin acids, are removed with a pipet and transferred to a second 100 cc. cylinder. After the addition of 20 cc. of dilute hydrochloric acid solution (1 part of acid to 2 parts of water), the whole is shaken. The ethereal layer is drawn off, and the water solution is shaken twice more with ether. The ether extracts are united and washed free from acid with water, and the ether is distilled. The residue, which consists of the resin acids, is dried to constant weight at 110° to 115° C.

Determination of Paraffin Hydrocarbons in Simple Rubber Compounds

In the case of rubber compounds the acetone extract of which contains only free sulfur and vulcanization accelerators (in addition to solid and liquid paraffin hydrocarbons), a separation of the acetone-soluble constituents into saponifiable and unsaponifiable parts is not necessary. For the determination of the paraffin hydrocarbons, the acetone extract is treated at once with 30 cc. of absolute alcohol, and the solution is filtered into a dry, weighed 200 cc. Erlenmeyer flask containing chips to prevent bumping. The filter and the flask (which contained the acetone extract) are washed with 20 cc. of hot absolute alcohol, using small portions at a time. The Erlenmeyer flask, which should now contain all of the alcohol-soluble substances of the acetone extract, is preserved for 1 hour in an ice-salt mixture at a temperature not above —5° C. The rest of the operation is carried out in exactly the same manner as described in detail under the heading "Separation of Constituents in the Unsaponifiable Portion of the Acetone Extract" (*see* p. 364). In this method for the determination of solid as well as liquid paraffin hydrocarbons, any sulfur which is present must be determined according to the method described on page 361, and must be subtracted from the value obtained.

[30] See Tuttle, J. B., "The Analysis of Rubber," p. 70, Chemical Catalog Company, New York, 1922; also see Allen, "Commercial Organic Analysis," 4th ed., Vol. V, p. 73, P. Blakiston's Son & Co., Philadelphia, 1910.

Identification of Organic Accelerators of Vulcanization

A quantitative determination of the organic accelerators in vulcanizates is at the present time seldom made. Moreover, the determination, when carried out, is only approximate. The determination can only be made when the accelerator undergoes no fundamental change at vulcanization temperatures, and when it can be separated from the rubber compound by steam distillation, sublimation, etc. Even the qualitative detection or identification of such compounds is among the most difficult problems of rubber analysis, many of which have not yet been satisfactorily solved. On the one hand, the analytical investigation is made difficult by the complexity of the chemical nature of the accelerators and by the fact that they are present in rubber compounds in such small quantities. Moreover, many accelerators, as has already been mentioned, undergo very fundamental changes during vulcanization, and later disappear entirely from the rubber compound. Conclusions regarding the presence of an accelerator in rubber goods can therefore only be drawn from the mechanical properties of the vulcanizates, the remarkably small quantity of total sulfur, and the vulcanization coefficient. Although the number of accelerators used in practice is very small in comparison with the large number of substances which are listed in the patent literature, the complete identification of the accelerator in a given compound is only possible in very favorable cases. The reason that so few of the many proposed accelerators are actually used in the rubber industry is to be found in the fact that most of the compounds described in the patent literature do not possess the properties listed below, which L. E. Weber [31] states are required of an accelerator that is to be used commercially.

1. The accelerator must not make the compound dry (short).
2. The critical temperature at which the accelerator begins to exert its accelerating action must not lie below 105° C., since otherwise the danger exists that the rubber compound will be prematurely vulcanized on the mixing rolls. Obviously, this does not apply to the so-called ultra accelerators, in the use of which special precautionary measures must be taken.
3. The accelerator should not discolor the vulcanizate.
4. The accelerator should not be toxic.
5. The accelerator must be obtainable on the market at a suitable price.

Among the compounds which fulfill the above requirements, and which have become commercial in Germany, those of the I. G. Farbenindustrie are of primary importance. The products of this company, which appear on the market under the designation of Vulkacit accelerators, include the following:

Hexamethylenetetramine (Urotropin, "Vulkacit H"; in America, "Hexa").
Aldehyde-ammonia ("Vulkacit A").
Diphenylguanidine ("Vulkacit D"); in France, "Nurac"; in America, "D. P. G."; or in a mixture with zinc oxide or magnesium oxide, "Speed X" or "X. L. O.").
Diphenylthiourea (Thiocarbanilide, "Vulkacit CA").
Piperidinium pentamethylenedithiocarbamate ("Vulkacit P"; in America, "Pip-pip").
Tetramethylthiuramdisulfide ("Vulkacit Thiuram"; "Tuads").
Di-ortho-tolylguanidine ("Vulkacit 1000"; in America, "D. O. T. G.").

Among the above accelerators, diphenylguanidine is today perhaps the most widely used in Germany. Furthermore, mention should be made of the following Vulkacits, the chemical nature of which is not definitely known:

"Vulkacit TR," a liquid basic mixture.
"Vulkacit BP," a salve-like basic mixture with formaldehyde.

[31] *India Rubber J.*, **63**, 793, 849 (1922).

In foreign countries, the following products have found extensive use in addition to the above:

In America: Triphenylguanidine ("T. P. G."), and "Tensilac," presumably a mixture of ethylidene-aniline and di-*o*-tolylguanidine.*
In England: Nitroso compounds, such as nitrosobenzene and nitrosophenol, as well as para-nitrosodimethylaniline. (Under the designation "Accelerene").
In France: Formaldehyde-aniline ("Vulcone") and "Super-Sulfur No. 2 (lead dimethyldithiocarbamate).

The following compounds are also to be listed among accelerators: Zinc alkyl xanthogenates, zinc alkyl dithiocarbamates, zinc thiophenol, dithiobenzoic acid, and the fatty acids, such as oleic and stearic acid, which act as accelerators at vulcanization temperatures when in combination with basic inorganic compounds.

Many of these accelerators pass into the acetone extract of the rubber compound, as they are either soluble in the original form or decompose into products soluble in acetone. At the conclusion of the acetone extraction, which is carried out as previously described (*see* p. 359), the solution should be evaporated to about one-half its volume, and then allowed to stand over night. If certain accelerators are present large crystals occasionally separate on standing. These can be recognized by their crystalline form, or, after careful purification, by means of their melting points and other properties.[32] Unfortunately, however, the conditions are seldom favorable to crystal formation, and other methods for the identification of these accelerators must be used.

If the list of accelerators cited above is examined, it will be noted that many of them contain 12 to 25 per cent of nitrogen. Since such nitrogen-containing compounds are soluble in acetone, the presence of an accelerator of this type in a rubber compound can be recognized by a nitrogen determination of the acetone extract. However, every sample of crude rubber contains nitrogen compounds which are partly soluble in acetone. The nitrogen content of the acetone extract of the most frequently used Hevea plantation rubbers averages 0.03 per cent. In the case of the wild rubbers it is usually somewhat higher. From experience it has been found fairly safe to conclude that an accelerator is present, if the nitrogen content of the acetone extract of a rubber compound appreciably exceeds the value of 0.06 per cent. It must be pointed out, however, that in recent years antioxidants (or "preservers") are added to the rubber to resist the aging of vulcanizates. Amongst these, certain ones, such as aldol-*alpha*-naphththylamine, phenyl-*beta*-naphthylamine, and other secondary amines, also contain nitrogen and are soluble in acetone. They can be recognized by mechanically testing the artificially aged rubber sample.

The micro-method of Bang or of Gerngrosz and Schäfer[33] can be used to advantage for the nitrogen determination of the acetone extract. The procedure is as follows:

The hot acetone extract is transferred immediately after the completion of the extraction to a micro-Kjeldahl flask of about 100 cc. capacity (Fig. 57), and the solvent is distilled on the water bath. To the residue

* Translator's Note. Included among other accelerators which find extensive use in America are mercaptobenzothiazole and its derivatives, and some of the faster aldehydeamines, such as butyraldehyde-aniline, ethylidene-aniline and heptaldehyde-aniline.

[32] *Cf.* T. Callan and N. Strafford, *J. Soc. Chem. Ind.*, **43T**, 1 (1924).

[33] *Z. angew. Chem.*, **36**, 391 (1923).

are added 3 to 4 drops of a 10 per cent copper sulfate solution, together with 5 cc. of concentrated sulfuric acid. The mixture is heated over a free flame until the liquid becomes clear.

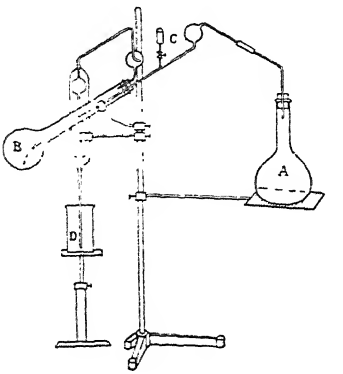


Figure 57—
Micro-Kjeldahl apparatus.

During the time of decomposition, the boiling flask *A* (250 cc.) is filled with about 100 cc. of water, which has been slightly acidified with dilute sulfuric acid. Several porous tile chips are also added to the flask to prevent bumping. The water in flask *A* is now vigorously boiled, and the steam is passed for several minutes into a second micro-Kjeldahl flask which has been inserted into the assembled apparatus. This procedure is necessary in order to flush out the apparatus before inserting the Kjeldahl flask containing the decomposed sample. The rubber connection between flask *A* and the delivery tube is broken and 4 cc. of 0.1*N* sulfuric acid are added to the beaker *D*, which is adjusted so that the end of the delivery tube dips beneath the surface of the liquid. The empty Kjeldahl flask *B*, which has been used up to this time, is then exchanged for the one which contains the decomposed sample and to which has been previously added distilled water (about 10 cc.) sufficient to permit the steam delivery tube to dip beneath the surface of the liquid. The funnel *C*, which is provided with a glass stopcock, is then filled with 50 per cent sodium hydroxide solution, and, by opening the stopcock, the solution is allowed to flow into the flask *B* until a black precipitate of copper oxide appears (about 2 to 5 cc.).

The apparatus is now connected to the steam generator *A*, which has been kept in operation, and the ammonia in the Kjeldahl flask is carried into the beaker *D* by means of a strong current of steam. During the entire operation, it is essential to have a rapid stream of cold water flowing through the condenser. The time of distillation varies with the ammonia content of the solution in the Kjeldahl flask. Even when several milligrams of nitrogen are present, the distillation never requires more than 10 minutes, and is not to be continued longer than is necessary. In order to determine whether or not the distillation has been completed, the support is lowered, the tube is rinsed, and the end of it is touched with a strip of red litmus paper. Should this turn blue, the necessity of further distillation is indicated. In this case, the litmus paper is thoroughly rinsed, the washings being retained in the beaker.

The titration of the contents of the receiving vessel *D* is carried out with a microburet; that is, a capillary tube of about 2 to 3 cc. capacity, graduated

in hundredths of a cubic centimeter, and filled from below by means of a funnel tube connected to the buret with a stopcock. In order to obtain accurate results, it is preferable to make but one filling of the buret, and to provide the solutions to be titrated with the necessary indicator before each determination. One must also be certain that the reagents which are used are free from nitrogen. This is especially true in the case of the sulfuric acid which is used for blank determinations. The stopcock of the microburet must not be greased, because the introduction of grease into the capillary causes a highly undesirable retention of drops.

The titration can be carried out iodometrically by titrating with sodium thiosulfate (using starch as the indicator) the iodine liberated according to the following reaction:

$$5\,KI + KIO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 6I$$

The excess of sulfuric acid can also be determined volumetrically, using 0.1*N* sodium hydroxide and methyl orange as the indicator.

In addition to the nitrogen content, attention must also be given to a possible metal content of the acetone extract. The presence of metals can be readily established by careful ashing.

If the presence of an accelerator has been established, the procedure of D. F. Twiss and G. Martin [34] for the recognition of its nature is followed.

Nitroso accelerators are recognized by the characteristic color of the acetone extract. In the presence of para-nitrosodimethylaniline, the acetone extract is colored yellow to dark brown, depending on the quantity of this substance present. If this accelerator is present, boiling of a rubber sample with dilute hydrochloric acid (1:2) under a reflux condenser produces an acid liquid, which, when treated with a small quantity of a solution of hydrogen sulfide and a solution of iron chloride, gives a blue to green color. The acetone extract also gives the same reaction. During vulcanization, para-nitrosodimethylaniline yields some para-aminodimethylaniline, which in the course of the above described treatment is converted to methylene blue. Nitroso compounds can further be detected by taking up the dried acetone extract with dilute hydrochloric acid and allowing the solution to react with metallic zinc for a short time. In this operation, the nitroso compounds are reduced to aromatic amines which, after being diazotized and coupled with phenols, yield red or blue colored solutions or precipitates.

Aldehyde-ammonia derivatives (hexamethylenetetramine and similar compounds) are detected by extracting a rubber sample under a reflux condenser with water, and testing the resulting solution for ammonia with Nessler's reagent. In addition, 5 grams of rubber are boiled for several hours under a reflux condenser with dilute hydrochloric acid (1:2). A portion of the filtered acidic liquid is treated with sodium hydroxide until an alkaline reaction is obtained, the resulting solution is subjected to distillation, and the distillate is tested for ammonia or volatile amines. A positive reaction for the above substances indicates the presence of furfuramide, hydrobenzamide, alkylamines, alkylammonium-dithiocarbamates, or urea. Another portion of the filtered acidic liquid is carefully tested by smelling of it. If accelerators of the thiocarbanilide type are present, the characteristic odor of phenyl mustard oil (phenyl isocyanate) is detected. If this odor cannot be

[34] *Gummi-Ztg.*, **35**, 1151 (1921); also J. B. Tuttle, "The Analysis of Rubber," p. 94, Chemical Catalog Co., Inc., New York, **1922**.

detected, the liquid is cooled in an ice bath and diazotized with a cold dilute solution of sodium nitrite. A test portion of this mixture is then shaken with a solution of *beta*-naphthol dissolved in an excess of sodium hydroxide. If the liquid is colored red or a red precipitate is produced, primary amines are present; that is, in the rubber compound there are present free aromatic bases such as aniline, toluidine, para-phenylenediamine, or derivatives of such bases, such as their condensation products with aldehydes (anhydroformaldehyde-aniline or formaniline, methylene aniline, and benzylidene aniline) or with carbon bisulfide (of the type of thiocarbanilide). Substances such as triphenylguanidine must also be considered.

Even though the above analytical scheme is satisfactory in many cases, the situation is frequently complicated by the fact that pure accelerators are not always used, but rather mixtures which are prepared by heating organic bases with sulfur. The fact that accelerators of the dithiocarbamate type, which are prepared from alkylamines by heating with carbon bisulfide, are destroyed at vulcanization temperatures, has previously been mentioned.

A method * which is useful not in the analysis of rubber compounds but rather for the identification of organic accelerators when available in their commercial forms is that of K. Shimada [*J. Soc. Chem. Ind., Japan*, **36**, Suppl. binding 82 (1933); *Rubber Age (London)*, **14**, 275 (1933)]. The method depends on the fact that most accelerators give colored complexes with organic cobalt salts. In the procedure used, 0.05 gram of the purified sample is dissolved in 10 cc. of benzene, and several drops of a one per cent solution of cobalt oleate in benzene are added. The reader is referred to the original article for information regarding the different colors formed when various accelerators are present.

As discussed in the section on microscopy, many accelerators can also be identified by the colors which they exhibit when exposed to filtered ultra-violet light. (*See* page 643.)

Rubber Resins

An approximate value for the content of so-called "rubber resins," which seem on the basis of our present knowledge to be only remotely related to actual resins (*see* p. 315), can be obtained by difference in the case of a simple rubber compound. The values which have been determined for the individual constituents of the acetone extract are added, and the sum is subtracted from the value obtained in the determination of the acetone-soluble constituents. In the case of complex rubber mixtures, it is a futile task to attempt to calculate even an approximate value for the resin content.

Determination of the Chloroform-soluble Constituents

The acetone-extracted rubber sample, without being dried, is immediately extracted with chloroform for 4 hours in the extraction apparatus in the same manner as previously described for the determination of the acetone-soluble constituents (*see* p. 359). The solvent is then distilled on the water bath, and the flask, together with the residue, is dried to constant weight in an oven at 100° C.

If the chloroform extract exhibits fluorescence, or if the color is darker than straw-yellow, the rubber material contains bituminous substances. Asphaltic substances and tar products may be present, if they have not already gone into solution in the treatment with acetone. The contents of the flask are then boiled with normal benzine and allowed to stand 12 hours. The

* Translator's Note.

solution is filtered, and the flask, as well as the filter, is washed several times with small portions of benzine. The residue on the filter is redissolved in the flask with warm benzene, the solvent is evaporated, and the flask and contents are dried in an oven at 100° C. to constant weight. The substances insoluble in benzine are termed hard asphalt.

In connection with the chloroform extract, it must be remembered that soft rubber goods, even when normally vulcanized, are dissolved by chloroform in small quantities. According to experience, 4 to 5 per cent,[35] based on the pure rubber content, can be dissolved. If this limit is exceeded and the presence of bituminous substances cannot be detected by the color of the chloroform extract, considerable quantities of rubber have gone into solution. This indicates either that the sample being tested has not been vulcanized to the proper degree, that it contains reclaimed rubber, that it has been damaged by excessive mechanical working during the process of manufacture, or that it is badly aged.

If bituminous substances are to be determined in unvulcanized rubber compounds, the material must be vulcanized before the extraction with chloroform.

Extraction with 0.5 *N* Alcoholic Potassium Hydroxide

Alcoholic potassium hydroxide dissolves the major portion of the oxidized fatty oils and the white and brown factice from the rubber sample, which has already been extracted with acetone and chloroform. In addition, the proteins (naturally occurring substances accompanying the rubber hydrocarbon), casein, wool, and portions of phenolic resins are dissolved.

The rubber sample, after having been extracted with acetone and chloroform, is dried at 50° to 60° C. and is treated, immediately after drying, with 50 to 100 cc. of benzene in a 200 cc. Erlenmeyer flask.[36]

After standing for at least 12 hours, 50 cc. of a hot alcoholic potassium hydroxide solution (approximately 0.5 *N*) are added to the warm swollen rubber, and the mixture is boiled from 4 to 6 hours under a reflux condenser. The rubber is then separated from the solution by filtration, and is washed, first with hot absolute alcohol and later with hot water, until no further extraction takes place. This washing operation is carried out by squeezing and pressing the rubber in a porcelain mortar. The united washings are combined with the filtrate and evaporated almost to dryness. The residue is taken up with about 100 cc. of water, is transferred to a separatory funnel, and, after being acidified with dilute sulfuric acid, is extracted with ether as long as portions of the water solution are extracted by the ether. The united ether extracts are freed from acid by washing with water, and are then evaporated to dryness in a weighed Erlenmeyer flask provided with chips to prevent bumping. The flask containing the residue is dried to constant weight in an oven at 100° C.

The approximately 0.5 *N* alcoholic potassium hydroxide is prepared by dissolving 30 grams of potassium hydroxide (purified by means of alcohol) in an equal quantity of water, cooling, and diluting the solution to 1000 cc. with absolute alcohol.

[35] According to J. B. Tuttle ("The Analysis of Rubber," p. 71, Chemical Catalog Co., Inc., New York, 1922), normally vulcanized, unoxidized soft rubber contains from 1 to 3 per cent of chloroform-soluble constituents.

[36] The "standard" extraction apparatus without the syphon cup (*see* p. 360) can be used to advantage for this purpose.

For the determination of the sulfur combined with organic compounds in the potassium hydroxide-soluble portion of the rubber sample, the procedure followed is the same as that used for the determination of the sulfur content of the acetone extract (*see* p. 361). It is to be observed that the oxidation with nitric acid-bromine mixture alone is not sufficient, but that the second or third procedure must be followed, since otherwise the danger arises that some sulfur combined as sulfonic acids will escape precipitation with barium chloride.

As already mentioned, the alkali extract also contains proteins. In order to calculate approximately the quantity of the oxidized oils or white and brown factice, the approximate protein content must be known. This is obtained by determining the nitrogen content of the alkali-soluble portion of the rubber compound by the micro-Kjeldahl method previously described (*see* p. 369), and multiplying the resulting value by the figure 6.25. By subtracting this value from the total quantity of the alcoholic potassium hydroxide extract, the value for the approximate content of oxidized oils or white and brown factice in the rubber sample can be obtained (taking into account the fatty acids and oleic acid found in the acetone extract).

Phenolic resins cannot be determined quantitatively. Their presence is recognized by the odor of the alkali-soluble constituents.

Determination of the Total Quantity of Pigments* and Other Fillers

In the simplest method for determining the pigment content, the weighed sample (1 to 2 grams) is ashed in an open crucible. The crucible (of about 45 cc. capacity) is placed on an asbestos mat containing a hole about 15 cm. in circumference. The bottom of the crucible is heated cautiously with a small Bunsen flame until no more decomposition products of the rubber escape, after which it is ignited at red heat on a clay triangle to constant weight.

Obviously this simple procedure is only applicable if the rubber compound contains no substances which are volatile or are changed under these conditions. Combustible substances, such as carbon black and cellulose, are not determined in this way. Moreover, many commonly used inorganic compounds suffer extensive changes in the ashing process. Thus, for example, sulfides are converted into oxides, carbonates split off carbon dioxide and cinnabar volatilizes completely. For this reason, in the determination of the total quantity of pigments in soft rubber goods, methods involving the solution of the vulcanized rubber are usually employed.

In carrying out the determination by this method, one gram of acetone- and chloroform-extracted rubber is dried at 50° to 60° C. and is immediately placed, together with 25 cc. of "liquid paraffin D. A. B. 6" or petroleum (the fraction boiling at 230° to 260° C.), in a dry, weighed flask of about 200 cc. capacity, provided with an air condenser. The mixture is heated with constant vigorous stirring until all of the rubber has gone into solution. After cooling, the flask is nearly filled with benzene and allowed to stand 24 hours

* Translator's Note. The word "pigment" as used throughout this section does not carry the same significance as in the paint industry, for instance, but refers rather to a finely divided compounding ingredient for rubber. Examples of pigments are gas black, zinc oxide, whiting and other reinforcing and non-reinforcing ingredients. Although the word "pigment" is commonly employed in the rubber industry, its [illegible] in the literature is avoided by many writ- appears times in the section be as a Dispersing Med..... which was translated by

in order to permit the finely divided pigments to settle. The supernatant liquid is then decanted and filtered with suction through a dry, weighed Gooch crucible provided with a double filter plate and a long-fibered asbestos filter bed. The filtrate is poured back over the filter repeatedly until it runs through perfectly clear. The contents of the flask, as well as the residue on the Gooch crucible, are repeatedly washed with hot benzene until the filtrate is no longer colored. The washing is then repeated several times with alcohol and ether, and the flask and the Gooch crucible are dried in an oven at 100° C. If the equipment is available, it is more desirable to centrifuge the suspension several times and decant the solution each time than to filter it. The paraffin-oil or petroleum solution of rubber is diluted to 100 to 130 cc. with benzene, and the solution is centrifuged about 20 minutes. The clear liquid above the pigments, which cling to the bottom of the vessel, can now be poured off. The residue in the flask is boiled with benzene, and the precipitate on the bottom of the flask is stirred during the boiling. The suspension is again centrifuged. Moreover, the entire centrifuging process may be repeated once or twice. Finally, the residue is washed with petroleum ether, alcohol, and ether, and the flask and its contents are dried.

In addition to the use of paraffin oil and petroleum, the separation of the vulcanized rubber from the pigments present can also be carried out in an autoclave, with xylene, according to Frank and Marckwald.[37] It must be mentioned that in the methods described above certain discrepancies in the results may arise from the formation of colloidal solutions in the presence of heavy metal compounds, especially lead sulfide. The formation of colloidal solutions can be recognized by the dark color of the solutions of vulcanized rubber after filtering or centrifuging. In order to determine the quantities of such pigments (which quantities are in general very small) the solutions are evaporated on the sand bath in a porcelain crucible, and are then ashed carefully.

If the rubber compound contains pigments, such as antimony pentasulfide, which decompose at the temperatures required for the solution of the vulcanized rubber in the liquids mentioned above, anisole may be used as the solvent. This liquid dissolves the rubber at 100° to 120° C. Since the presence of antimony pentasulfide makes the filtration of the solution very difficult, the separation of the pigments after dilution with ether is accomplished by centrifuging. It is to be emphasized, however, that the use of anisole is inadvisable when the rubber samples contain litharge, since the formation of lead phenolate leads to errors in the results.

If the compound contains highly dispersed (exceedingly fine) pigments, the above solution methods are not applicable, since a separation of these pigments is usually not possible by means of filtration or centrifuging. In certain cases, the method of ashing in nitrogen, which was proposed by Goldberg, gives rapid results. This method can also be used to advantage with hard rubber samples.

One gram of the dried acetone- and chloroform-extracted rubber sample is weighed into a porcelain boat, which is placed in a combustion tube through which a rapid stream of pure dry nitrogen is passed, in order to displace the air. The ashing is carried out in the nitrogen by first heating that part of the combustion tube behind the boat (towards the end of the tube at which the gas leaves) with a Bunsen wing-top burner, then cautiously and progressively continuing the heating of the space ahead of the boat, and finally

[37] *Gummi-Ztg.*, **22**, 134 (1908).

heating the boat itself with two more wing-top burners. All unnecessary overheating of the tube is to be avoided. The ashing is complete as soon as no more vapors are carried out by the nitrogen. To facilitate the flow of the gases, the combustion tube is placed in a slightly inclined position. The porcelain boat is allowed to cool in a stream of nitrogen, and the quantity of the remaining residue is determined by weighing.

Since all of the above-described methods for the determination of the total quantity of pigments in the rubber samples are carried out on acetone- and chloroform-extracted rubber, the results must be recalculated to convert them to the basis of the original sample.

In cases in which none of the above-described processes are applicable, the individual pigments must be separately determined according to the methods to be described.

Sulfur Determination

Total Sulfur

For the determination of the total sulfur of a rubber compound, the method of J. Rothe is most suitable.

One gram of the rubber sample to be analyzed is placed in a 200 to 250 cc. round-bottomed Pyrex flask containing 1 gram of magnesium oxide, and is treated with 30 to 40 cc. of nitric acid (specific gravity 1.48). The oxidation is started by warming on the water bath. In the case of compounds containing only small quantities of pigments, it is advisable to treat the sample first with dilute nitric acid (or a mixture of dilute and concentrated nitric acid) on the water bath, and then to add the concentrated acid. The contents of the flask are kept at incipient boiling by moderate heating of the flask on the sand bath for 1 to 2 hours. At the end of this time the excess of acid is evaporated over a free Bunsen flame, while the flask is continuously rotated. The residue is further heated over a single burner, and later over a triple burner, until brown fumes are no longer liberated. The residue must contain no carbonized portions. If such are present, the treatment with nitric acid must be repeated. After oxidation, the contents of the flask are taken up with 5 cc. of concentrated nitric acid and diluted with water, and the undissolved substances are filtered.

After evaporating the filtrate to dryness in a porcelain evaporating dish, the residue is dried for two hours in an oven at 135° C., moistened with concentrated nitric acid, and taken up with water. After filtering off any insoluble substances, the filtrate is evaporated to dryness in a porcelain dish, and is then evaporated three times to fumes with 5 cc. portions of concentrated hydrochloric acid. The residue is finally taken up with 5 cc. of concentrated hydrochloric acid. After diluting with water to about 100 cc., the solution is treated at the boiling temperature with hot barium chloride solution and is allowed to stand over night. The precipitated barium sulfate is filtered, washed free from chlorine, ashed, and weighed. In the case of rubber samples with a high sulfur content, it is advisable to dilute the solution containing sulfate to a volume of 250 to 500 cc. before precipitating with barium chloride, and to use only a portion of this liquid for the sulfur determination. With rubber compounds which contain no antimony and no silicates which would decompose under the conditions described above, the procedure can be correspondingly simplified.

The insoluble residue remaining after the decomposition (according to the method of Rothe) is carefully ashed in a crucible placed on an asbestos wire screen, and the ash is fused with five to six times its weight of sodium potassium carbonate. The fused mass is taken up with hot water, and the solution is filtered. The filtrate is acidified with nitric acid and evaporated to dryness, and the residue is heated for 2 hours in a drying oven at 135° C. Nitric acid is added, and the solution is diluted with water and filtered to free it from any silicic and antimonic acids. The filtrate is evaporated to dryness in a porcelain dish, further evaporated three times to fumes with hydrochloric acid, and is then taken up with hydrochloric acid. The sulfuric acid contained in the solution is finally determined in the manner described above.

A number of methods * for the determination of total sulfur have recently been described. A method based on the oxidation of the sample with perchloric acid has been proposed by E. Wolesensky [*Ind. Eng. Chem.*, **20**, 1234 (1928); *Rubber Chem. Tech.*, 2, 45 (1929)]. The procedure is as follows:

"To a 1-gram sample of the finely divided or crumbled rubber in a 500 to 800 cc. Pyrex Kjeldahl flask (the larger size is preferable) add 10 cc. of a 41 per cent solution of nitric acid (1 volume concentrated acid and 1 volume water) and heat on a steam bath for 1 or 2 minutes until brown fumes appear and the reaction has subsided. Then add 10 cc. of concentrated nitric acid and continue heating for about 15 minutes more until the rubber is nearly or entirely dissolved. Add 5 cc. of a 60 per cent solution of perchloric acid, set the flask in an inclined position on asbestos gauze, and heat with a burner to gentle boiling until dense white fumes appear and the solution (in absence of insoluble inorganic compounds) is clear and colorless or nearly so. At this point it may be necessary to add more perchloric acid (3 to 5 cc.) if free carbon is present, or, in absence of other precipitates, the carbon may be filtered off later. When all organic matter has been oxidized, allow to cool somewhat, add slowly 5 cc. of concentrated hydrochloric acid, and once more heat until white fumes appear, then allow to cool for a few minutes and wash into a beaker. If the solution is clear it may be heated at once (after diluting to about 200 cc.), treated with barium chloride, and the precipitate separated and weighed as barium sulfate in the usual manner. If the original free carbon of the rubber has not been completely oxidized, and it is known that no other insoluble matter is present, the carbon may be filtered off and the filtrate then treated for sulfates as before. If the liquor resulting from the oxidation of the rubber contains an insoluble residue, and it is known to be only barium sulfate, this may be filtered off, washed, ignited, and weighed as barium sulfate; or the insoluble residue, whatever its nature, may be filtered off, washed, dried, and fused with sodium carbonate, after which it is examined for sulfates, and possibly also for metals, according to the usual methods in such cases. Sulfates may also be extracted from any insoluble residue by boiling with sodium carbonate. In either event, however, the filtrate from such insoluble residue should always be treated for sulfates as above."

The determination of sulfur in rubber by means of the calorimetric bomb has been described by B. Saladini [*Giorn. chim. ind. applicata*, **13**, 409-441 (1931); *Rubber Chem. Tech.*, **5**, 216 (1932)]. The procedure is as follows:

"Weigh 0.1 to 0.3 gram of finely divided rubber directly in a platinum or a quartz crucible in the calorimetric bomb, add about 1 cc. of decalin, immerse an iron spiral in the liquid for the purpose of ignition, and after putting 10 cc. of distilled water in the bottom of the bomb, close the latter, fill it with oxygen to 30 atmospheres' pressure, and close the electric circuit.

"After the combustion is over, cool the bomb, allow the gas to escape slowly, and open the bomb after twenty to thirty minutes. It is not necessary to pass the gas into a solution of sodium carbonate to catch any sulfurous gas nor to oxidize it with bromine water and to add this liquid to the main solution, because oxidation is always complete. After the bomb is opened, wash it carefully with hot water, together with the crucible, and collect the wash waters in a 300 to 350 cc. beaker. Precipitate with ammonia the traces of iron present (the iron spiral and lining of the bomb are of special steel), filter, acidify with hydrochloric acid, and determine the sulfur gravimetrically as barium sulfate."

* Translator's Note.

Combined Sulfur in Mineral Pigments

For the determination of the sulfur present in inorganic compounds, a weighed quantity of the residue obtained from the pigment determination by the solution method (*see* p. 374) is transferred to the flask shown in the apparatus in Figure 58. The 10-bulb tube is provided with 50 cc. of a hydrochloric acid-bromine mixture,[38] and carbon dioxide is conducted through the apparatus for some time. The dropping funnel *A* is filled with concentrated hydrochloric acid, which is forced into the flask by opening the stop-cock at the bottom of the funnel and introducing carbon dioxide under pressure at the top. The dropping funnel is then filled with a mixture consisting of equal parts of concentrated hydrochloric acid and of hydrochloric acid having a specific gravity of 1.19. This acid mixture is transferred to the flask by the same method described above. After the evolution of hydrogen sulfide has subsided, the flask is slowly heated to the boiling temperature and boiled for some time. After the contents of the flask have been allowed to cool while passing a steady stream of carbon dioxide through the apparatus, the liquid in the bulb tube is washed into a beaker. The solution is concentrated, and the sulfuric acid formed is precipitated (while hot) with barium chloride solu-

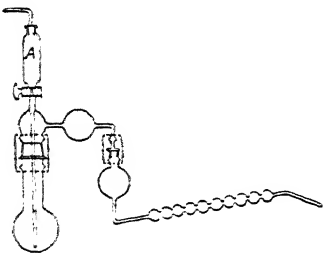


Figure 58—
Apparatus for sulfide-sulfur determination.

tion. If the residue from the pigment determination contains iron oxide, it is necessary to add a considerable quantity of stannous chloride or metallic zinc before the decomposition with hydrochloric acid.

The contents of the decomposition flask are filtered. The filtrate containing the soluble sulfates, after the addition of some sodium chloride, is evaporated to dryness. The residue is heated for 2 hours in a drying oven at 135° C., and is taken up with hydrochloric acid and water. The resulting solution is filtered. The sulfuric acid present in the filtrate is then precipitated with barium chloride. If antimony is present, it must be removed before precipitating the sulfates with barium chloride. The method for removing antimony was described under the determination of total sulfur by the Rothe method (*see* p. 376).

The acid-insoluble pigments, remaining after the decomposition with hydrochloric acid, are decomposed by fusing them with sodium potassium carbonate. The fused mass is extracted with hot water, and the alkaline solution is filtered and oxidized with hydrogen peroxide. The solution is then acidified with nitric acid and evaporated to dryness in a porcelain dish. The residue is dried in a drying oven at 135° C. for 2 hours. The procedure is then the same as that described for the insoluble residue under the determination of total sulfur (*see* p. 377).

[38] 13 grams of bromine in 1 liter of hydrochloric acid (specific gravity 1.13).

From the sum of the weights of barium sulfate obtained by the above operations, the total quantity of combined inorganic sulfur in the rubber compound can be calculated.

If only the total quantity of combined inorganic sulfur is to be determined, and there is no interest in distinguishing the sulfur present as sulfides from that present as sulfates, the following procedure can be followed:

A weighed quantity of the residue from the pigment determination according to the solution method (*see* p. 374) is mixed in a crucible with 4 to 5 times its weight of sodium potassium carbonate and a little sodium peroxide and is heated carefully until the mixture is entirely fused. The cooled mass is extracted with hot water and filtered, and the alkaline filtrate is oxidized with hydrogen peroxide. The solution is acidified with nitric acid and evaporated to dryness in a porcelain dish. The residue is dried for 2 hours in a drying oven at 135° C. The succeeding operations are carried out in the manner described for the insoluble residue of the total sulfur determination. (*See* p. 377.)

Sulfur Combined with Rubber

In rubber compounds which contain only sulfur and rubber, or compounds in which no sulfides or sulfates are present (either added as such or formed during vulcanization), the determination of the sulfur combined with the rubber is a relatively simple procedure. The rubber sample is extracted with acetone, and any factice present is removed with an alcoholic solution of potassium hydroxide. The sample, which has been washed free from alkali while being rubbed in a porcelain mortar, is analyzed according to the procedure for the determination of total sulfur (*see* p. 376).

In the case of complex rubber compounds, for which the above method is not applicable, the sulfur combined with rubber must be calculated by difference in the following manner:

The values obtained for free sulfur (*see* p. 361), for combined inorganic sulfur (*see* p. 378) and for sulfur in the alkali extract (*see* p. 374) are added, and the sum is subtracted from the value obtained for total sulfur (*see* p. 376).*

Determination of Selenium

For the determination of the selenium content, the process of E. H. Shaw and E. E. Reid [39] is followed. In this method, 0.5 to 1 gram of the rubber sample is mixed in a crucible with 0.5 gram of cane sugar, 0.2 gram of potassium nitrate, and 14 grams of sodium peroxide, and the mixture is covered with a thin layer of sodium peroxide. The mixture is fused in the usual manner. The cooled mass is dissolved in water. The solution, after filtration if necessary, is heated to boiling to destroy the excess hydrogen peroxide. After cooling, the solution is acidified with hydrochloric acid and diluted with water. The selenium is now present in the form of selenic acid, and can be determined as the element selenium in the following manner:

Concentrated hydrochloric acid is added to the solution, which is then covered with a watch glass and heated to boiling. Sulfur dioxide is led into the solution (which is hot but not boiling) until the precipitate has agglomerated into a lump and the supernatant liquid has become clear. After the water used in rinsing the watch glass has been added to the solution, the latter is further diluted and is then filtered through a Gooch crucible. The beaker

* *See* also method of W. J. Kelly, *India Rubber World*, **63**, 175 (1920); **65**, 491 (1922).

[39] *J. Am. Chem. Soc.*, **49**, 2330 (1927).

is freed from adhering selenium with alcohol. The contents of the crucible are washed first with alcohol, then several times with water, and are finally dried at 110° to 120° C. to constant weight.

In place of sulfur dioxide, the selenium can also be separated by means of potassium iodide. For this purpose, 50 cc. of concentrated hydrochloric acid and 3 grams of potassium iodide are added to the solution, which is then boiled gently until all the iodine is removed (2 hours). Evaporation losses are replaced with distilled water. Vigorous boiling of the solution is to be avoided. The precipitated selenium is filtered through a Gooch crucible as previously described, washed with alcohol and water, and dried at 110° to 120° C.

Determination of Chlorine

The determination of the chlorine content of cold-vulcanized rubber compounds, or of those containing white factice, is carried out according to the method of Henriques. One gram of the original sample is first fused with a mixture of saltpeter and soda (free from chlorine). The carbon-free mass is taken up with water, the solution is filtered, and the filter is washed with hot water. After the filtrate has been acidified with nitric acid and boiled, 25 cc. of a 0.1 *N* silver nitrate solution are added. The solution is brought once more to boiling, and the excess of silver nitrate is back-titrated by means of a 0.1 *N* ammonium thiocyanate solution, using ferric ammonium sulfate as indicator.

In the case of cold-vulcanized rubber samples, it is sometimes desirable to obtain an approximation of the amount of chlorine which is combined with the rubber, in addition to the amount which is present in the white factice. For this purpose the sulfur combined with the rubber is determined, as directed on p. 379 under "Sulfur Combined with Rubber." The equivalent chlorine content is calculated from this value.

Determination of Carbonic Acid

For the determination of the amount of carbon dioxide combined with mineral pigments, 3 to 5 grams of the original, finely divided rubber sample are decomposed in a flask by heating with a solution of hydrochloric acid containing mercuric chloride, while passing through the solution a stream of air free from carbon dioxide. The liberated carbon dioxide, after being passed through a calcium chloride tube, is collected in a potash bulb or soda lime tube and weighed.

In order to obtain better penetration of the rubber by the acid, Pearson[40] used acetic acid in place of hydrochloric acid for decomposing the carbonates. The first part of the apparatus proposed by him consists of a flask provided with a short reflux condenser. The condenser is connected to a U-tube containing solid lead acetate. This tube is followed by another U-tube, one arm of which is filled with sodium acetate, and the other with calcium chloride. The absorption of the carbon dioxide takes place in a soda-lime tube. During the entire determination, carbon dioxide-free air is passed through the apparatus.

[40] *Analyst*, **45**, 405 (1920).

Determination of Glue

The approximate quantity of glue in a rubber compound can be calculated either from the nitrogen content obtained by a Kjeldahl nitrogen determination (*see* p. 351) on the original sample, or, in the case of samples containing accelerators and antioxidants, from the results of a nitrogen determination on the acetone-extracted rubber sample. The rubber content of a sample must be known before the glue content can be calculated, since rubber always contains proteins as accompanying substances. The nitrogen content of the most widely used types of Hevea rubber varies between 0.3 and 0.6 per cent of the rubber. An average value of 0.5 per cent nitrogen can therefore generally be assumed. The small quantities of nitrogen compounds removed from the rubber during the extracting with acetone can be left out of consideration. From the total percentage of nitrogen thus determined is subtracted 0.5, which is the percentage originally present in the rubber sample. The result, when multiplied by 6.25 (the factor corresponding to the average nitrogen content of proteins), gives the approximate content of dry glue or gelatin in the rubber compound. In order to gain information regarding the type of glue present, the ash of the rubber sample is tested for phosphorus, which is to be found in considerable quantity when bone glue is used.

For the qualitative detection of glue, Epstein and Lange [41] heat the rubber sample with cresol at 120° C. for 16 hours, during which time the rubber goes into solution. The swelled mass is then diluted with petroleum ether. The glue and other insoluble substances are precipitated. After the supernatant liquid has been decanted, the residue is filtered through a Gooch crucible, washed with petroleum ether and hot benzene, and dried. The material thus prepared is boiled with water, and the filtered solution is tested with tannin.

In case the qualitative examination gives no evidence of the presence of glue and the nitrogen determination indicates larger quantities of proteins than are naturally present in the rubber, casein and leather flour may be present. Casein is detected by treating the acetone-extracted rubber sample, or the residue prepared according to the method of Epstein and Lange, with dilute ammonia or alkali, approximately neutralizing the solution, and applying the Adamkiewiz [42] test. In this test a solution of glyoxylic acid in concentrated sulfuric acid is added to the neutral solution to be tested in such a manner that the acidic solution forms a layer on the bottom of the tube. In the presence of casein, a stable violet color appears at the zone of contact. The presence of leather flour is confirmed microscopically in the pigments obtained according to one of the solvent methods (*see* p. 374).

Determination of Cellulose

Cellulose may be present in rubber goods in two forms,[43] either as cotton or other waste, or in the form of continuous fabric (as in rubber articles with fabric plies or in rubber-coated products).

If the ratio of fabric to rubber is to be determined, and later also the construction and the weight of fabric per square meter (or square yard), a

[41] *India Rubber World*, 61, 216 (1920).

[42] Allen, "Commercial Organic Analysis," 4th Edition, Vol. VIII, p. 40, P. Blakiston's Son & Co., Philadelphia, 1913; see also *J. Biol. Chem.*, 6, 51 (1906).

[43] For information concerning the determination of cellulose derivatives see page 364.

method is used which is very similar to the solvent method for determining pigments in rubber.[44] In the case of articles heavily coated with rubber, the first step is to remove the rubber (as completely as possible without injuring the fabric) from a sample of known dimensions and known weight. The sample thus prepared, or the original sample (in the case of fabrics less heavily coated) is heated with a high boiling petroleum fraction (230° to 260° C.) until the rubber has dissolved. If necessary the heating may be carried out in an autoclave with benzene, or preferably xylene. The fabric, after being washed with benzene and ether and then dried, retains between the threads certain pigments. It is therefore necessary to heat the fabric first with soda solution and then with dilute acetic acid, and finally to wash it thoroughly with water. The sample is then dried and weighed at 100° C. The cellulose is finally burned, the loss on heating being considered water-free cellulose. By adding 8.5 per cent to the value obtained, the results can be calculated to air-dried fabric. The method is obviously only applicable when the rubber compound does not contain combustible pigments such as carbon, or substances which contain chemically combined water or carbon dioxide. In these cases the methods described below, which are intended for the determination of finely divided cellulose in rubber compounds, must be used.

According to the method of Epstein and Moore,[45] a weighed sample of the rubber material is heated in a flask with freshly distilled cresol (boiling point 189°; 25 cc. to 0.5 grams of rubber sample) for 4 hours at 165° C. After cooling, 200 cc. of petroleum ether are carefully added with constant shaking, and settling is allowed to take place. The solution is then filtered through a dried, weighed Gooch crucible provided with asbestos,[46] and the flask is washed three times with petroleum ether. The residue is carefully washed with boiling benzene and acetone. The contents of the flask are treated with hot 10 per cent hydrochloric acid solution, and are then transferred to the Gooch crucible, where they are leached at least ten times more with 10 per cent hydrochloric acid. The material in the Gooch crucible is washed free from chlorine with boiling water, and is treated with small quantities of acetone until the filtrate becomes colorless. In the same manner the residue is treated with a mixture of equal parts of acetone and carbon disulfide, washed with alcohol, dried 1½ hours at 105° C., and weighed. It is still better to transfer the entire contents of the crucible, with the aid of pincers, to a weighed watch glass, using the lower part of the asbestos mat to wipe out the inside of the crucible. The whole is then dried 10 minutes longer, and after cooling is weighed. The weight of the material on the watch glass is designated as *A* (*see* next paragraph). After this preliminary treatment, the determination of the cellulose follows.

The contents of the watch glass are treated in a flask with 25 cc. of "Kuoxam."[47] After shaking frequently and allowing to stand for 12 hours, the solution is filtered through asbestos in a dried and weighed Gooch crucible. The contents of the crucible are first washed with concentrated and later with dilute Kuoxam solution, and finally with ammonia water until the filtrate passes through perfectly clear. The crucible is dried to constant weight at 105° C., and after cooling, is weighed. The difference between the

[44] See page 374; and Porritt, *J. Soc. Chem. Ind.*, **38**, 50 (1919).

[45] *India Rubber J.*, **59**, 559 (1920).

[46] The asbestos must be boiled previously with hydrochloric acid.

[47] *See* footnote 26 on p. 364, for directions in regard to the preparation of "Kuoxam."

weight of the empty Gooch crucible plus *A*, and the weight of the crucible after dissolving the cellulose with Kuoxam, gives the quantity of cellulose. As a check, the cellulose can be determined directly by adding sodium chloride to the Kuoxam solution which has been united with the wash waters, and precipitating with dilute sulfuric acid. The precipitated cellulose is filtered with suction through a dried, weighed Gooch crucible, washed with hot water to the disappearance of a chlorine reaction in the filtrate, dried at 110° C., and weighed.

The cellulose can also be determined according to the acetylization method. The contents of the watch glass are treated in a beaker of 50 cc. capacity with 15 cc. of acetic anhydride and 5 cc. of concentrated sulfuric acid, and are digested at least one hour on the steam bath. After allowing the mixture to cool to room temperature, 25 cc. of 90 per cent acetic acid are added, and the solution is carefully filtered through asbestos in a Gooch crucible by applying a slight suction. The residue is washed first with hot 90 per cent acetic acid, and finally five times with acetone. The crucible is dried for two hours at 150° C. and weighed (after cooling). The quantity of cellulose present is calculated in the manner described under the Kuoxam method.

Determination of Carbon Black

The determination of the carbon present in the form of carbon black is carried out according to a process developed by Smith and Epstein.[48] One-half gram of the original rubber sample is extracted for 8 hours with a mixture consisting of 1 volume of acetone and 2 volumes of chloroform. The sample is transferred to a 250 cc. beaker and is evaporated on the steam bath until the odor of chloroform has disappeared. The cooled sample is treated with several cubic centimeters of cold concentrated nitric acid, and is allowed to stand for a short time. After the addition of 50 cc. of hot concentrated nitric acid of specific gravity 1.40, the mixture is heated at least one hour on the water bath until no further evolution of gas takes place. The hot liquid is filtered through a weighed Gooch crucible, as much of the solids as possible being kept in the beaker. The contents of the beaker and of the Gooch crucible are washed with hot concentrated nitric acid. After emptying the suction flask, the washing is continued with acetone and with a mixture of equal volumes of acetone and chloroform until the filtrate becomes clear. The material in the beaker is now treated for 30 minutes on the water bath with 30 to 40 cc. of a 35 per cent solution of sodium hydroxide. This operation can be omitted if no silicates are present in the rubber sample. The solution is diluted with 60 cc. of hot distilled water and filtered through the Gooch crucible. After washing the beaker thoroughly with hot 15 per cent sodium hydroxide solution, the residue is tested for the presence of lead by pouring a warm solution of ammonium acetate, containing excess of ammonia, through the Gooch crucible, and allowing the resulting solution to flow into a sodium chromate solution. If lead is present, the residue, which is quantitatively contained in the crucible, is washed with a hot solution of ammonium acetate until the solution coming through no longer causes a turbidity in the sodium chromate solution. Thereupon the residue is washed several times with hot concentrated hydrochloric acid, and finally with warm 5 per cent hydrochloric acid. The Gooch crucible and contents are dried for 1½ hours at 110° C., and, after cooling, are weighed. After burning off the

[48] *Ind. Eng. Chem.*, **11**, 33 (1919).

carbon at a dull red heat, the crucible is again weighed. The difference in weight represents approximately 105 per cent of the original quantity of carbon in the form of lamp black or gas black. The resulting value is therefore divided by 1.05 to give the per cent of black present.

Determination of Graphite

For the determination of the graphite content of a rubber sample, 0.5 to 1 gram of the sample is boiled for 4 hours with 0.5 *N* alcoholic potassium hydroxide solution. After filtering, the filter paper and the residue are transferred to a small porcelain dish and evaporated four times to fumes with nitric acid of specific gravity 1.52. The dried residue is mixed with about ten times its weight of lead oxide, transferred to a Hess clay crucible, covered with a layer of lead oxide, and heated in the covered crucible over the blast lamp until evolution of gas ceases. After cooling, the crucible is broken and the lead regulus found on the bottom is weighed.

$$\frac{\text{The weight of the lead regulus}}{34.5 \times \text{the weight of the sample}} \times 100 = \% \text{ free carbon.}$$

Carbon black, if present in addition to the graphite, is also determined by this procedure.

Quantitative Determination of the Inorganic Constituents

Survey

The following inorganic constituents may be contained in rubber compounds:

Antimony pentasulfide (Golden antimony)	Lead sulfate
Tin oxide	Zinc dust
Arsenic compounds	Zinc sulfide
Mercuric sulfide (Cinnabar)	Zinc oxide (Zinc white)
Lead oxide (Litharge)	Lithopone
Red lead	Iron oxide (Red oxide)
White lead (Basic lead carbonate)	Aluminum hydroxide (Clay)
Lead sulfide	Kaolin
Ultramarine	Pumice stone
Chalk or Whiting	Basic magnesium carbonate
Lime	Powdered glass
Calcium sulfate (Gypsum)	Silicic acid (Infusorial earth and sand)
Barium sulfate (Barytes or blanc fixe)	Asbestos
Magnesia usta (Calcined magnesia)	Talc

Before the determination of the individual inorganic constituents of a rubber compound can be undertaken, all organic substances must first be removed. This is best done by utilizing the method of J. Rothe, which avoids the volatilization of certain individual constituents, such as arsenic, antimony and mercury.

The weight of the rubber sample for analysis is chosen to give about 1 gram of ash. The weighed rubber sample is placed in a 300 cc. Pyrex round-bottomed flask, together with 10 to 20 cc. of nitric acid of specific gravity 1.48 and 2 cc. of concentrated sulfuric acid for each gram of rubber material, and is heated on the sand bath for about one hour at a temperature just sufficient to bring about a constant lively evolution of nitrogen dioxide. The flask is then heated more strongly on the sand bath until the nitric acid has been com-

pletely evaporated, and fumes of sulfuric acid come from the liquid. The heating is continued over a free flame, with vigorous shaking of the flask, until the sulfuric acid boils. The flask is allowed to cool, is inclined, and to the warm sulfuric acid is added 5 to 10 cc. of nitric acid (specific gravity 1.48). The heating is continued for 1/4 to 1/2 hour on the sand bath with moderate boiling, until the liquid, which is usually colored dark brown or black, has become clear. The heating is then continued anew over the free flame until the sulfuric acid boils strongly. A dark color should not develop during the boiling. If this happens to be the case, nitric acid must be added again and the procedure repeated. When the sulfuric acid finally remains clear on boiling, the main quantity of the acid is evaporated over a free flame, and the concentrated solution, after cooling, is taken up with water. The sample to be tested has now been prepared for analysis.

The Insoluble Residue

Any insoluble residue remaining after the decomposition (according to the method of Rothe) is filtered and thoroughly washed. It may contain such substances as the sulfates of lead, calcium and barium, silicic acid or silicates, antimonic acid and lead antimoniate, and occasionally stannic acid. The separation and determination of these substances is described below.

Lead. The insoluble residue is boiled several times with a solution of ammonium acetate in order to separate the lead sulfate, the operation being repeated until the filtrate no longer gives a dark coloration with hydrogen sulfide. The residue on the filter is then washed with hot water and is preserved for further analysis (compare the procedure described for barium). In the ammonium acetate solution, which may contain small quantities of gypsum in addition to the lead sulfate, the precipitation of the lead is accomplished with hydrogen sulfide, and the precipitate is filtered and washed with hydrogen sulfide water. The filtrate is evaporated to dryness in a porcelain dish. After the ammonium salts have been removed by heating, the residue is dissolved in hydrochloric acid, and any calcium present in the solution is determined in the manner to be described later. (*See* p. 389.)

The lead sulfide is dissolved in hot nitric acid. The solution, after the addition of sulfuric acid, is evaporated, and the excess of sulfuric acid is removed on the sand bath. The residue is taken up with 1 per cent sulfuric acid, and, after standing overnight, is filtered. The lead sulfate is washed with 1 per cent sulfuric acid. The filter is then carefully ashed in a porcelain crucible. The ashing is conducted by first placing the crucible on an asbestos wire screen and heating it until the paper is completely carbonized, then transferring the crucible to a clay triangle, and finally heating with a free flame until all carbon has been burned. Excessive heating is to be avoided in order to prevent reduction and volatilization of the lead. If the residue is not pure white after ashing, it is evaporated on the water bath with several drops of concentrated nitric acid, treated with several drops of concentrated sulfuric acid, evaporated to fumes on the sand bath, and then heated over a small flame until the bottom of the crucible reaches a dull red heat. The above operations are repeated until the weight of the crucible becomes constant. The purity of the lead sulfate is verified by treating it with hot ammonium acetate solution. Any insoluble residue remaining after this treatment is filtered, thoroughly washed, heated to redness, and weighed. Its weight is subtracted from the weight of the lead sulfate.

Barium. The residue remaining after the removal of the lead sulfate is ashed in a Rose crucible, and the ash is mixed with 5 or 6 times its quantity of a mixture consisting of equal parts of sulfur and sodium carbonate. The decomposition is accomplished by heating the bottom of the crucible carefully from below with a small flame, and the cover and later also the sides from above, by fanning with a large Bunsen flame. The heating is continued as long as sulfur continues to burn between the cover and the crucible. The decomposition is finished when no more sulfur clings to the inside of the cover or on the walls of the crucible. After cooling the crucible with the cover on, the fused mass is taken up with water, and the solution is filtered. The filter contains lead sulfide, barium carbonate, and calcium carbonate, as well as silicic acid and silicates which were not attacked by the moderate heating employed during decomposition. The filtrate contains antimony and occasionally tin. This solution is saved to be worked up later with the main quantity of the antimony (*see* p. 387).

The residue on the filter is treated with hot dilute hydrochloric or nitric acid, whereby lead, barium, and calcium go into solution, while silicic acid or the silicates remain undissolved. The residue, after ashing and fusing with sodium potassium carbonate, is tested for the presence of bases which must be determined as such in the course of the analysis. Silicic acid is best determined on a separate sample of the rubber. (*See* p. 389.)

The acid solution is treated with hydrogen sulfide after dilution or neutralization. Any precipitated lead sulfide is converted to lead sulfate in the manner described under lead (*see* p. 385), and is weighed as such. After expelling the hydrogen sulfide from the filtrate remaining after the hydrogen sulfide precipitation, the barium is separated from the calcium. When small quantities of calcium are present, the barium is separated as sulfate. In the presence of larger quantities of calcium, it is best separated as the chromate.

The Filtrate from the Decomposition (According to Rothe's Method)

Mercury. The solution remaining after the decomposition (according to the method of Rothe) is treated with hydrogen sulfide. This precipitates antimony and the elements rarely occurring; namely, arsenic, tin and mercury. If mercury is present, the precipitate is colored black. In this case the residue, after being transferred to a beaker with a little water, is treated with a hot dilute solution of sodium hydroxide, whereby the sulfides of antimony, arsenic, and tin go into solution. The insoluble mercuric sulfide is dissolved in aqua regia. After boiling off the chlorine from the solution, the mercury is precipitated with hydrogen sulfide. The mercuric sulfide is separated from the solution by passing the latter through a dried weighed Gooch crucible. The residue is thoroughly washed, dried and weighed.

Arsenic. The alkaline solution containing the arsenic, antimony, and tin is acidified with hydrochloric acid and treated with hydrogen sulfide. The residue is filtered, washed thoroughly with weakly acidic hydrogen sulfide water, and transferred to a beaker. The sulfide mixture is warmed with concentrated hydrochloric acid, which dissolves the antimony and tin. The insoluble arsenic sulfide, after thorough washing, is dissolved with aqua regia, precipitated as magnesium ammonium arsenate by means of ammonia, ammonium chloride and magnesium sulfate, and weighed as magnesium pyroarsenate.

Antimony. The solution containing antimony and tin is united with

the solutions which were obtained from the decomposition of the insoluble residue (*see* p. 386) and which also contain antimony and tin. The latter solutions, however, contain sodium sulfide and must first be treated with sodium hydroxide and cooled. Bromine is then added a drop at a time until all of the sulfur is oxidized. After the solution is acidified and the bromine expelled, the two solutions are united. Antimony and tin are separated by bringing the solution to boiling and adding during the course of one hour 0.5 to 1.0 gram of *ferrum reductum* in small portions. After the reduction is completed, the antimony is immediately filtered through a small filter covered with *ferrum reductum* and is thoroughly washed with hot dilute hydrochloric acid. In the presence of larger quantities of tin, the antimony must again be dissolved by warming with hydrochloric acid-bromine mixture (*see* p. 378). After removing the bromine by boiling, the reduction with *ferrum reductum* is repeated in order to complete the separation of the antimony. The filtrate in each case is tested by adding *ferrum reductum* to the boiling solution to determine whether the antimony has been completely removed.

The filtered antimony is transferred from the filter to a beaker with hot water and is dissolved with the mixture of hydrochloric acid and bromine. In the same way, antimony residues are washed from the filter with warm hydrochloric acid-bromine mixture. After evaporating the bromine, a small quantity of potassium iodide is added, and the solution is reduced with the aid of heat by adding sulfurous acid a drop at a time, care being used to avoid adding an excess. After most of the excess hydrochloric acid in the solution has been neutralized with ammonia, the antimony is precipitated with hydrogen sulfide, and the separated antimony sulfide filtered and washed with boiled water. The sulfide is then washed through the filter into a beaker by means of 50 cc. of a warm 25 per cent solution of sodium sulfide. The filter is washed with 50 cc. of 25 per cent sodium sulfite solution, and a piece of sodium hydroxide, the size of a pea, is added to the filtrate. After the hydroxide has dissolved, the solution is electrolyzed with the aid of a weighed platinum gauze electrode at 60° C., using at first a current of 0.5 ampere, and after 1 hour a current of 1 ampere. After passing the current through the solution for 2 hours, some sodium sulfite solution is added, and an observation is made to determine whether any antimony precipitates on the freshly wetted part of the cathode. If none is deposited, the electrode is quickly removed from the solution without interrupting the current, washed for several seconds with hot water, dried with alcohol and ether, and weighed.

When only small quantities of antimony are present, the sulfide is dissolved with warm freshly prepared yellow ammonium sulfide. The solution is evaporated in a weighed porcelain crucible, and the residue is further evaporated with concentrated hydrochloric acid, care being exercised to avoid losses by spattering. The sulfuric acid produced is evaporated to fumes on the sand bath, and the antimony, after ignition, is weighed as Sb_2O_4.

The antimony can also be determined by titration. In this case, the antimony, after being separated from the tin and precipitated as the sulfide (by means of hydrogen sulfide), is transferred to a Kjeldahl flask, and is carefully heated with 15 cc. of concentrated sulfuric acid until the solution has become colorless. The solution is diluted to 100 cc., 1 to 2 grams of sodium sulfite are added, and the resulting solution is boiled until all sulfur dioxide has been expelled. The solution is then treated with 20 cc. of concentrated hydrochloric acid, diluted with water to a volume of 250 to 275 cc., and

titrated with a 0.1 *N* solution of potassium permanganate to a slight red coloration. The permanganate solution[49] is standardized by heating 0.25 gram of pure metallic antimony in a 600 cc. Erlenmeyer flask with 12 to 15 cc. of concentrated sulfuric acid and 10 to 12 grams of potassium sulfate until solution is complete. After adding 25 cc. of water and 20 cc. of concentrated hydrochloric acid the solution is diluted to 270 cc. After being cooled to 10° to 15° C. the solution is titrated to a faint pink color with the permanganate solution.

Tin. Hydrogen sulfide is passed into the filtrate from the antimony-tin separation (*see* p. 387), which contains the tin in the stannous form. The resulting tin sulfide is filtered and ashed in a Rose crucible. In this operation the crucible is heated on an asbestos wire screen until the filter paper has charred, and the carbon is then burned on a clay triangle over a small Bunsen flame. The crucible is finally heated to glowing, first over a Bunsen burner, and later over a blast lamp. The tin is converted to stannic acid in this manner and is weighed as such.

Zinc. The filtrate from the hydrogen sulfide (*see* p. 386) precipitation of mercury, antimony, arsenic, and tin is freed from hydrogen sulfide by boiling. This solution is first made alkaline by the addition of ammonia, and is then acidified with sulfuric acid,[50] or preferably with formic acid. Hydrogen sulfide is then passed into the liquid. The precipitated zinc sulfide is allowed to stand overnight (under a bell jar) and is filtered the next day through a filter containing paper pulp. The zinc sulfide is washed with hydrogen sulfide water, containing some ammonium sulfate or acetate and a small quantity of sulfuric or formic acid. The filter and precipitate is ashed in a Rose crucible in the manner described under "Tin." After ignition, the resulting zinc oxide is weighed.

Iron Oxide, Aluminum Oxide, and Chromium Oxide. The filtrate from the zinc sulfide precipitation is freed from hydrogen sulfide by boiling. A little nitric acid is added to oxidize the iron to the ferric state and the chromium to the chromic state, and the boiling solution is made alkaline with ammonia. The precipitated hydroxides are filtered, washed with hot water, ignited and weighed. The weighed mass consists of iron oxide, aluminum oxide, and chromium oxide. The contents of the crucible are then transferred to a platinum dish and fused with sodium hydroxide, to which has been added a very small quantity of sodium peroxide. The fused mass, after cooling, is treated with water, which dissolves the aluminate and chromate but not the iron hydroxide. The latter is thoroughly washed, and then dissolved in dilute hydrochloric acid. The iron content of the solution, after addition of potassium iodide and starch, is determined by titration with 0.1 *N* normal sodium thiosulfate solution.[51]

The filtrate containing the sodium aluminate and chromate, is acidified with hydrochloric acid, and is likewise treated with potassium iodide and starch. The chromate content is determined by titration with 0.1 *N* sodium thiosulfate.[52]

The sum of the calculated quantities of iron oxide and chromium oxide is subtracted from the total weight of the three oxides. The difference gives the amount of aluminum oxide.

[49] 3.1 grams of $KMnO_4$ dissolved in 1 liter of water. The solution is filtered through ignited asbestos after standing.

[50] The solution should react just acid toward methyl orange.

[51] 1 cc. of 0.1 *N* $Na_2S_2O_3$ = 0.007984 g. Fe_2O_3.

[52] 1 cc. of 0.1 *N* $Na_2S_2O_3$ = 0.00253 g. Cr_2O_3.

Calcium. After the precipitation of the iron, aluminum and chromium oxides, the filtrate is evaporated to about 100 cc., is then made weakly acid with acetic acid, and is treated at the boiling temperature with a hot solution of ammonium oxalate. After boiling for a few minutes the solution is treated with ammonia. Upon standing overnight, the precipitate is filtered, and, together with the filter paper, is ashed in a platinum crucible. The crucible and its contents are ignited over a blast lamp to constant weight.

Magnesium and Alkalies. The filtrate from the precipitation of calcium, after being acidified with sulfuric acid, is evaporated to dryness. After the residue has been freed from ammonium salts by moderate ignition, it is taken up with slightly acidulated water and filtered. The resulting solution is evaporated in an ignited and weighed platinum crucible, with the addition of sulfuric acid. The excess of sulfuric acid is driven off by heating on an asbestos wire screen, and the sulfates of the alkali metals and magnesium are then carefully ignited over a Bunsen burner and weighed.

The weighed sulfates are taken up with water, the clear solution is made strongly ammoniacal, and the magnesium is precipitated with ammonium phosphate. The precipitate, after standing overnight (under a bell jar), is filtered, washed with water containing ammonia, ignited to magnesium pyrophosphate, and weighed as such. The resulting value is calculated to magnesium sulfate, and this value is subtracted from the total weight of the sulfates obtained before removing the magnesium. The difference represents the alkali sulfates, which are calculated to sodium oxide.

Silicic Acid. One gram of the original rubber sample is ashed in a platinum crucible. The residue is thoroughly mixed with 4 to 5 times its weight of sodium potassium carbonate, and is decomposed by fusing over a Bunsen flame. The fused mass is leached with hot water, and the insoluble matter is removed by filtration and washed on the filter until free from alkali.

After the filtrate has been acidified with hydrochloric acid, it is evaporated to dryness. The residue is dried in an oven at 135° C. for 2 hours, then moistened with 5 cc. of concentrated hydrochloric acid, and finally taken up with hot water. The resulting insoluble silicic acid is filtered, washed well, ignited in a platinum crucible, and weighed. To determine the purity of the ignited residue, it is treated with 1 or 2 drops of concentrated sulfuric acid, and a sufficient quantity of hydrofluoric acid to volatilize the silicon as SiF_4. The hydrofluoric acid is then evaporated on a water bath, the sulfuric acid is driven off by heating over an asbestos wire screen, and the crucible is ignited and weighed. Any remaining residue is subtracted from the previous weight of silicic acid.

In rubber compounds containing lead, antimony and zinc, the ashing in a platinum crucible is not advisable, because of the danger of injuring the crucible. In this case, the silicic acid is determined in the above manner during the course of the analytical procedure previously outlined (*see* p. 386).

DETERMINATION OF THE RUBBER CONTENT

The rubber content of a sample is usually calculated. The sum of the

determined percentages of moisture, acetone extract,[53] hard asphalt in the chloroform extract, inorganic and organic pigments, alkali extract,[54] sulfur combined with the rubber, and chlorine are subtracted from 100 per cent. The difference is the pure rubber hydrocarbon, free from rubber resins and saponifiable constituents (except for those non-rubber constituents which frequently cannot be determined in complex rubber compounds).

Another method for the determination of the rubber hydrocarbon, proposed by the United States Joint Rubber Insulation Committee,[55] is only applicable in the case of compounds free from bitumen, cellulose, carbon black, mercuric sulfide, and other substances insoluble in hydrochloric acid but volatile or undergoing fundamental change during ashing. According to this method, the rubber sample, after being extracted with acetone, chloroform and alcoholic potassium hydroxide, is suspended in 125 cc. of water and treated with 25 cc. of concentrated hydrochloric acid. The whole is heated for 1 hour at 97 to 100° C. The supernatant liquid is decanted and filtered with suction through a Buchner funnel provided with a sheet of hardened filter paper. The residue is washed with 25 cc. of hot water, and the solution is again decanted and filtered. This treatment with water and hydrochloric acid is performed three times. At the conclusion of this treatment the rubber should be white and practically free from black specks. If this is not the case, the acid treatment is repeated until the black specks have disappeared. The residue is treated with 150 cc. of hot water and allowed to stand one-half hour on a steam bath. The solution is again decanted through the filter. Any rubber particles on the filter are then returned to the flask, and the washing with water is continued until the filtrate is free from chlorides. All of the rubber is transferred to the filter, and is dried by suction as much as possible. The rubber is next washed with 50 cc. of 95 per cent alcohol with the aid of suction, and is dried for one hour on a weighed watch glass at 95° to 100° C. The residue is allowed to cool in a vacuum desiccator under reduced pressure, and is then weighed. This process is repeated until the dried residue remains constant in weight or begins to increase in weight. About 0.5 gram of the residue is then transferred to a weighed porcelain crucible and ashed (*see* p. 374). In another portion of the rubber sample the sulfur is determined by the method described under "Total Sulfur" (*see* p. 376). The values obtained for ash and sulfur are then calculated to the basis of the acid-extracted sample, and subtracted from the weight of the latter. The difference gives the rubber hydrocarbon expressed as a percentage of the starting material.

Even though the methods thus far described for the determination of the rubber hydrocarbon are "difference" methods, there has been no lack of attempts to make possible the direct determination of the rubber in vulcanizates. For a determination by a direct method, however, the conditions are even more unfavorable with vulcanizates than with crude rubber. Critical examination of the methods described in the literature has shown them to be much less practicable than those with crude rubber. Furthermore, there appears to be no basis for hoping that they can be

[53] If possible, allowance is made for the "rubber resins."

[54] The weight of the proteins determined in the acetone extract is subtracted.

[55] *J. Ind. Eng. Chem.*, **9**, 310 (1917).

transformed into practical methods. However, in some cases the methods for direct determination offer an opportunity for checking the results of the indirect analysis. For this reason, two examples of the methods followed in the direct determination of the rubber hydrocarbon are presented below.

The reaction involving the addition of bromine to the rubber hydrocarbon was used by Axelrod [56] as the basis for a direct method for the determination of the rubber hydrocarbon. One gram of the acetone-extracted sample is dissolved in 100 cc. of petroleum (fraction boiling below 300° C.). After cooling and while vigorously shaking, 10 cc. of the solution are removed with a pipette and transferred to a 300 cc. beaker. To this solution are added 50 cc. of a brominating liquid (containing 6 cc. of bromine and 1 gram of iodine in each liter of carbon tetrachloride). The resulting white precipitate is allowed to stand for 3 or 4 hours to permit clarification and settling, after which 100 to 150 cc. of 96 per cent alcohol are added with stirring. After the solution has again been allowed to settle, the precipitate is transferred to a filter and is washed, first with a mixture of alcohol and carbon tetrachloride (1:1), and then with alcohol. According to the method of Axelrod, the filter and contents are dried at 60° C., weighed, and then ashed; and the residue is subtracted from the weight of the bromide.

Since this method is not free from errors, it was modified by Hinrichsen and Kindscher.[57] According to the modified method, the residue on the filter is dried at 40° C. and is dissolved in chloroform. The filter is then thoroughly washed with chloroform. The bromide in the filtrate is precipitated with benzine or alcohol, filtered, washed thoroughly with alcohol and warm water, and finally dried with alcohol and ether. The filter containing the bromide is then decomposed with sodium potassium carbonate (as described under "Crude Rubber"; *see* p. 353), and the bromine content is determined. In another sample of rubber bromide prepared in the same manner, the sulfur content of the bromide is determined by fusing with sodium potassium carbonate with the addition of sodium peroxide, since all of the sulfur combined with the rubber is present in the bromide. The result obtained for combined sulfur is then calculated to bromine, according to the equation, $S : 2\,Br =$ sulfur found : x, and this value is added to the previously determined bromine content of the bromide. The calculation of the rubber hydrocarbon from the bromine content is made in the manner described under "Crude Rubber" (*see* p. 353).

According to observations made by Hinrichsen and Kindscher, the tedious operation with petroleum can be avoided. Since the rubber bromide is soluble in chloroform, 0.1 to 0.3 gram of the acetone-extracted vulcanizate is swelled in chloroform (according to their procedure). Bromine is added, and the mixture is cooled in ice and allowed to stand until the pieces of rubber have disappeared and the pigments cover the bottom of the glass vessel as a fine powder. The treatment of the bromide contained in the chloroform solution is then carried out in the manner described above.

The nitrosite process described under the investigation of crude rubber (*see* p. 354) has also been suggested for the determination of the hydrocarbon

[56] *Gummi-Ztg.*, **21**, 1229 (1907).

[57] *Chem.-Ztg.*, **36**, 217, 230 (1912); see also Hübener, *Chem.-Ztg.*, **33**, 648, 662 (1909).

content of vulcanizates. According to the proposal of P. Alexander,[58] 0.5 gram of the finely divided, acetone-extracted rubber sample is suspended in carbon tetrachloride and allowed to stand overnight to permit swelling. A stream of nitrous gases is passed into the carbon tetrachloride, the gases having been prepared from starch and nitric acid (specific gravity 1.4) and purified by means of glacial phosphoric acid. The reaction product is formed within a short time, so that after several hours the swelled rubber pieces are completely transformed into the nitrosite. To make certain that the reaction is complete, the pieces are allowed to stand overnight in the solution saturated with nitric acid. The solid particles can then be pressed to a fine powder without difficulty. If, however, elastic rubber particles are present, the process of passing the gas into the solution must again be repeated. After the reaction is complete, the carbon tetrachloride is poured off, and the product is washed with the swelling solvent and superficially dried. The residue is then dissolved in acetone and filtered, and the filter is washed with acetone. The acetone solution is evaporated in a stream of hydrogen at a temperature not exceeding 40° C., only small portions of the solution being transferred to the flask at a time. After the major portion of the acetone has been removed by distillation, ether is added, according to a suggestion of Frank and Marckwald. Upon the addition of the ether, most of the reaction product precipitates as a powder, in which form it can be easily dried. The solvent and precipitating agents are then distilled, and the residue is dried in a current of air or hydrogen and weighed. The product is then used for the sulfur determination, since all of the sulfur combined with the rubber is in the reaction product. The quantity of sulfur determined is subtracted from the total weight of the nitrosite. Each gram of pure rubber is equivalent to 2.4 grams of the sulfur-free reaction product.

In connection with the nitrosite method, it has been pointed out by Tuttle[59] that the process of Wesson, as modified by Tuttle and Yurow, is the only accurate method for the direct determination of the rubber hydrocarbon which leads to practical results. Complete details regarding this method were given under the discussion of the analysis of crude rubber (*see* p. 354).

The Coefficient of Vulcanization

In order to obtain comparable figures for the degree of vulcanization of various rubber samples, the ratio of the combined sulfur of the sample to the pure rubber hydrocarbon is calculated. The calculation is made according to the following equation:

$$x = \frac{100a}{b}$$

in which a represents the per cent of combined sulfur in the sample, and b the per cent of rubber hydrocarbon in the mixture. The vulcanization coefficient has recently been of special interest, since it is possible, from its size, to draw conclusions regarding the presence or absence of vulcanization accelerators in vulcanizates, even when such agents cannot be detected in the finished product.

[58] *Gummi-Ztg.*, 21, 727 (1907).
[59] J. B. Tuttle, "The Analysis of Rubber," p. 79, Chemical Catalog Co., Inc., New York.

Physics of Rubber

By L. Hock*

Introduction

The exact determination of the physical constants of any substance demands first of all a knowledge as to whether these constants depend only upon the substance and its purity or whether they may be affected by the state of the substance as determined by previous history or other circumstances. The necessity of this, even for substances which are simple and chemically well-known, is at once apparent if we recall the existence of allotropic forms in crystalline substances or if we consider the technical preparation of metals. It can be seen, therefore, what must be the difficulties in determining the physical properties of rubber. On account of the multiplicity of its colloidal forms, there is plainly no preparation of rubber which is identical with another throughout, aside from the fact that chemically pure rubber has not been available for most investigations. This indefiniteness must be taken into consideration in interpreting the remarkable physical properties which confront the research worker as well as the practical technician. The indefiniteness, unfortunately, goes so far that a given preparation may behave differently according to the method of its preparation, so that great care is required to avoid unintentional variations of either a temporary or permanent nature in the material.

We must conclude from the above facts that, unfortunately, a large number of quantitative determinations of the properties of rubber which have been made in the past century are, in a way, useless as a basis for further work, because the workers have not described their preparations sufficiently well. In some cases it is not even possible to tell whether crude rubber or vulcanized rubber was used or whether the compound was reinforced by pigments or not. Many authors were accustomed to state at most the colors of the samples which were used, a fact of no importance.

If indeed there is no other alternative than to accept these uncertainties, these preliminary remarks must be kept in mind, and it must not be expected that rubber is a material upon which precision measurements can be made. It should also not be surprising to find that the measurements of different observers will not give particularly good agreement, and it should be remembered that results of duplicate investigations may differ by 10 or 20 per cent even under the same conditions. However, the indefiniteness which prevails in the experimental work at present will not always stand in the way of fundamental knowledge, so that it thus appears possible—against which the feeling of the exact scientist may instinctively rebel—to apply the methods of rigorous research to the stubborn problem of rubber if its solution is not to be renounced entirely.

* Translated by Norris Johnston, J. H. Howey and N. A. Shepard.

The Properties of Solid Rubber in the Unvulcanized and in the Vulcanized States

The Elastic Properties of Rubber

Reversible Deformations

Hooke's Law. The resistance which rubber offers to a change in the arrangement of its particles by a force from without is small, and when the stress ceases the particles return again to their original positions. This behavior manifests itself in what is known in everyday speech as the great elasticity of rubber. It exists, however, as a strictly reversible phenomenon only within quite a narrow limit, which in general extends further for highly vulcanized than for unvulcanized rubber. According to the fundamental law of elasticity (Robert Hooke, 1660) the amount of deformation per unit length is proportional to the acting stress: *"ut tensio, sic vis."* Complete elasticity exists insofar as the same force corresponds to a given elongation at any time both during the loading and the unloading of the deformable body. The elastic limit has been exceeded if the original state is not exactly regained after the load is removed, thereby leaving a permanent deformation or set. In the sense of everyday speech, elastic substances, of which rubber is an outstanding example, allow a considerable deformation before the elastic limit is exceeded. The period of time involved plays an important part in all elastic * strains, and particularly in the case of rubber this fact must not be disregarded. Rubber, especially in the unvulcanized state, shows a marked elastic after-effect which will be considered more in detail later.

Modulus of Elasticity. If a strip of rubber of length l and cross section q is elongated by an amount Δl when loaded with a weight p, the relation between these quantities according to Hooke's law is

$$\Delta l = \alpha\left(\frac{lp}{q}\right) \text{ or in differential form } dl = \alpha\left(\frac{ldp}{q}\right) \qquad (1.$$

The proportionality factor α is known as the coefficient of elasticity. If l be measured in meters, q in square millimeters and p in kilograms, the coefficient of elasticity thus defined is obviously equal to the elongation that is produced in a strip one meter long and one square millimeter in cross section by a load of one kilogram. The force which is required to double the original length ($\Delta l = l$) when the cross section equals one square millimeter may be used as a measure of the deformability, assuming that the deformation does not exceed the elastic limit. This condition may actually be reached with vulcanized rubber, but with other materials, such as steel for example, the case of $\Delta l = l$ can only be imagined. The force defined by the condition $\Delta l = l$ is the reciprocal of the coefficient of elasticity and is known as the modulus of elasticity $E(=1/\alpha)$. This physical measure of the elasticity leads to a definition which is directly opposed to the meaning of the word as used in everyday speech. According to this technical definition, the elasticity of vulcanized rubber ($E =$ .08 approx.) is less than that of steel ($E = 22{,}000$). Henceforth, use will be made of the term "modulus of elasticity," and the technical meaning of the term must be kept in mind.

* Translator's Note. The word elastic is evidently here used in an approximate sense, since the elastic relation as defined by Hooke's law is, strictly speaking, not a function of the time. J.H.H.

In the numerous older works are found determinations of the modulus of elasticity of rubber compounds (vulcanized threads, etc.). E. Villari [1] was one of the first to investigate this subject. We are indebted to W. C. Röntgen [2] for more careful and critical work with measurements which were intentionally limited to relatively small elongations. Above all, he bore in mind that with increasing length there was a decreasing cross section and a correspondingly increasing force per unit area. The technique of the method of measurement used by L. Bouchet [3] is of interest. The modulus of elasticity was determined by deformations which were produced by the application of manometrically measured hydrostatic pressure upon a cylindrical rubber body. Pressures of from 1x0.2 to 7x0.2 mm. of water were applied in loading and unloading cycles of from 2 to 4 minutes' duration. Corresponding deformations could also be produced by electrostatic means. (*See* p. 471.)

The modulus of elasticity is found to be dependent upon the amount of the elongation, and this dependence becomes more marked as the elastic limit is passed. It must be recognized, however, that when the elastic limit is passed we can no longer speak of the modulus of elasticity in the sense defined by Hooke's law. The results obtained by Villari at least make possible a survey of the existing values of the modulus. He determined the average values of the modulus in each of three regions of elongation as follows: for elongations of the rubber samples up to twice the original length, the value of E was 0.07 to 0.1; for further elongations, the modulus rose from 0.1 to 300; for elongations of more than 300 per cent, the modulus had an approximately constant value of from 300 to 350. P. V. Bjerkén [4] found the modulus to be 0.095 for rubber bands elongated to four times their original length. A. E. Lundal [5] obtained E=0.10 for "pure" rubber, taking into account the decrease in cross section. O. Frank [6] found E=0.089. Lundal also allowed his rubber test pieces to absorb 139 per cent of paraffin oil and found that the modulus fell to half of its original value. Possibly these examples are sufficient. A detailed compilation of the older literature may be found in the work of A. Slingervoet Ramondt, "Zur Geschichte der Kautschukforschung."[7] No attempt at historical completeness can be made here; rather only a selection from all the available works will be found in this and in the following sections. Recently G. B. Deodhar and D. S. Kothari [8] have investigated the dependence of the modulus of elasticity upon the elongation, finding a linear increase up to the breaking point of the rubber test piece. Even if the usual stress-strain relationship held for rubber the same as for other substances, rubber would still be peculiar in that the magnitude of its modulus throughout the whole course of elongation is vastly different from that of most substances.

A detailed study of the stress-strain curve for rubber has been made by C. W. Shacklock* [*Inst. Rubber Ind., Trans.*, **8,** 568, and **9,** 94 (1933); *Rubber Chem. Tech.*, **6,** 486, 504 (1933)], who has described the location of the point of inflection, and the relationship between elasticity and structure. Shacklock points out that application of the Hatchek correction for diminution in cross-sectional area does not entirely eliminate the point of inflection of the stress-strain curve, so the inflection point may properly be considered as

[1] *Ann. Physik*, **143,** 88 (1871).
[2] *Ann. Physik*, **159,** 601 (1876).
[3] *Compt. rend.*, **158,** 1495 (1914).
[4] *Ann. Physik*, **43,** 817 (1891).
[5] *Ann. Physik*, **66,** 741 (1898).
[6] *Ann. Physik*, [4], **21,** 602, (1906).
[7] Ramondt, A. Slingervoet, "Zur Geschichte der Kautschukforschung," Steinkopff und Springer, Dresden, **1907.**
[8] *Indian J. Physics*, **2,** 305 (1928); see also *Chem. Zentr.*, **99,** I, 2875 (1928).
* Translator's note by N. J.

an inherent property of the stress-strain relation of rubber. A mathematical deduction of the stress-strain curve equation is attempted.

The stress-strain curve of ebonite has been studied by B. L. Davies [*Trans. Inst. Rubber Ind.*, **9**, 130 (1933)]. (*See* p. 628.)

Poisson's Ratio. On account of the great change in form which rubber experiences under the action of rather small forces, it is important for us to consider somewhat more thoroughly the transverse contraction of elongated strips. With increasing elongation, the cross section of the strip always becomes smaller. The relation between the force p, acting on a strip of cross section q, and the decrease in the width of the strip Δb (in meters) is given in a form similar to equation (1) by

$$\Delta b = \frac{\beta b p}{q} \text{ or in differential form by } db = \frac{\beta b dp}{q} \tag{2}$$

where b is the original width of the strip and β is the coefficient of transverse contraction. If the stretching force is exactly 1 kg./mm.^{2} and the original width 1 meter, β is the decrease in width in meters.

The two coefficients α and β clearly determine the elastic behavior of a body. Taken together, the ratio of β to α is known as Poisson's Ratio μ':[9]

$$\mu' = \frac{\beta}{\alpha} \tag{3}$$

Poisson's ratio thus represents the ratio of the transverse contraction to the lengthwise extension. It can easily be related to the change in volume during elongation to give the so-called coefficient of volume increase under tension:[10]

$$\Phi = \alpha\ (1 - 2\mu') \tag{4}$$

Obviously, when $\mu' = 0.5$ there is no change in volume, which is exactly the case in the deformation of fluids. It is of interest that this relation is approximately fulfilled by rubber, although to a lesser extent than by gelatin, for example. Considerable departures from this relation occur, moreover, at high elongations, and there exists no constant volume throughout the course of the elongation. This is particularly true for unpigmented raw rubber. The relationship here discussed deals only with the more or less ideal elastic properties within the elastic limit, which are to be observed in high quality, vulcanized compounds. Under these conditions, all deformations can be calculated from the modulus of elasticity and Poisson's ratio insofar as they are produced by the action of any force on a presumably isotropic solid body. The assumption of elastic isotropy means that the rubber test piece will react in the same manner elastically in all directions. An example in which this condition would not be satisfied is a piece of rubber which has been markedly elongated in one direction so that it has become anisotropic. (*See* pages 416 and 420.)

The value of Poisson's ratio for vulcanized rubber has been investigated by many workers. Wertheim,[11] Villari,[12] Röntgen,[13] Bjerkén,[14]

[9] For details of the fundamental ideas of elastic theory see Vol. 3 of "Handbuch der Experimentalphysik," by W. Wien and F. Harms, Akad. Verlags-Gesellschaft m. b. H., Leipzig, **1928**.

[10] The simple derivation of this equation can be found in complete physics texts, such as those of Müller-Pouillet, Chwolson, and others.

[11] *Ann. Physik*, **78**, 381 (1849).

[12] *Ann. Physik*, **143**, 297 (1871).

[13] *Ann. Physik*, **159**, 601 (1876).

[14] *Ann. Physik*, **43**, 818 (1891).

Corbino and Canizzo[15] should be mentioned among those of the past century. Besides direct measurements of elongation and constriction, indirect measurements of the volume, i.e. of the specific gravity, have been used to determine the ratio. Among the later works of Lampe,[16] Frank[17] and others, the work of L. Schiller[18] is particularly noteworthy because of its careful attention to all experimental details. The works of Röntgen and of G. F. Becker[19] are also outstanding.

Poisson's ratio as defined by finite values of the transverse contraction and elongation obviously cannot represent a real material constant. Röntgen based his calculations, therefore, not on the original length and width, but on the instantaneous values of those quantities when the strip was in an elongated condition which differed only slightly from its final state. However, the value of Poisson's ratio for infinitely small elongations can be obtained from observations of finite lengths as shown below. According to the definition given in equation (3)

$$\mu = \frac{-db}{b} \cdot \frac{l}{dl} \tag{5}$$

where μ (unprimed) stands for the ratio as referred to differential changes in length, b the width, and l the length of the stretched rubber strip. Integrating between the limits of the original state and the final state, we have

$$\int_{b_2}^{b_1} \frac{db}{b} = \mu \int_{l_1}^{l_2} \frac{dl}{l} \qquad \text{or} \qquad \mu = \frac{\log \frac{b_1}{b_2}}{\log \frac{l_2}{l_1}} \tag{6}$$

In Table 1 are given some results for various elongations, obtained on a strip of vulcanized rubber 1.07 mm. in thickness.

TABLE 1.—*Determination of Poisson's Ratio (According to L. Schiller).*

No.	Elongation in per cent	$1000\,\mu$	b_1 (mm.)	b_2 (mm.)	l_2 (mm.)	l_1 (mm.)
1	2.3	457	10.487	10.376	258.5	252.6
2	7.4	453	10.262	10.148	271.4	264.8
3	10.1	462	10.137	10.919	278.5	271.5
4	78.3	500	9.300	7.999	390.6	289.0
5	102.1	472	10.342	7.420	243.9	120.7

The average value of twenty measurements for μ is 0.480 (dark Para sheet, specific gravity 0.95). The elongation and contraction were measured by means of marks made on the center of the elongated sheet. If the value of μ for infinitely small changes in form is known, it is possible to calculate from it the value of μ' which corresponds to Poisson's ratio for finite deformations.

From equation (6) it follows that:

$$\left(\frac{l_2}{l_1}\right)^{\mu} = \frac{b_1}{b_2}; \qquad b_1 - b_2 = b_1 \left(\frac{l_2^{\mu} - l_1^{\mu}}{l_2^{\mu}}\right) \tag{7}$$

[15] *Rend. Accad. lincei (Roma)*, **7**, 2nd half, 286 (1898).

[16] *Sits. Akad. Wiss. Wien*, **111**, IIa, 982 (1902).

[17] *Ann. Physik*, [4], **21**, 602 (1906).

[18] Dissertation, Leipzig, 1911; "Die Änderung der Dielektrizitätskonstanten des Kautschuks bei Zug senkrecht zu den Kraftlinien." Compare also: *Ann. Physik*, [4], **22**, 204 (1907).

[19] *Amer. J. Sci.*, [3], **46**, 348 (1893).

In analogy to equation (3), μ' may be expressed in terms of measured finite distances by the equation

$$\mu' = \frac{b_1 - b_2}{l_2 - l_1} \cdot \frac{l_1}{b_1} \tag{8}$$

Substituting from equation (7) we have the desired relation between μ' and μ,

$$\mu' = \frac{l_2^{\mu} - l_1^{\mu}}{l_2 - l_1} \cdot \frac{l_1}{l_2^{\mu}} \tag{9}$$

Conversely it follows:

$$\mu = \frac{\log [l_2 - \mu' (l_2 - l_1)] - \log l_1}{\log l_1 - \log l_2} \tag{10}$$

While μ is independent of the degree of elongation, μ' always becomes smaller with increasing elongation and falls from a value of 0.449 at an elongation of about 10 per cent to 0.115 at an elongation of 500 per cent. The data obtained by Schiller show remarkable agreement with the results of an earlier investigation by Bjerkén, which are given in Table 2.[20]

TABLE 2.—*Determination of Poisson's Ratio (According to Bjerkén).*

Loading p	Length l	Poisson's ratio μ'	Relative change in volume
0	44.2	.....	1.000
5	54.5	0.403	1.012
105	140.0	0.192	1.080
405	213.5	0.134	1.141
805	227.0	0.125	1.193
1005			

A value for μ' of 0.5 would indicate that rubber was like a practically incompressible fluid, a conclusion which was reached by earlier workers, Amagat,[21] Bouasse,[22] and others.

If there is no constant volume upon which to base deductions, and if the deformations are so large that the applicability of the equations is questionable, it may be concluded that for any considerable change in shape there is no corresponding change in volume which can be detected by such measurements as would ordinarily be used to determine the change in shape. It can therefore be said that the bulk modulus of rubber is very large in comparison to the modulus of rigidity.[23] In other words, it requires the application of a large force to change the volume while a slight force will alter the shape. If a rubber sheet be anisotropic as a result of the method of manufacture, Poisson's ratio may possess different values in two directions perpendicular to each other. In one case reported by Schiller the values of μ were 0.535 and 0.463 in different directions. The average value must be equal to or less than 0.5 because otherwise an increase in volume would result from tension. Such decreases in density have indeed been observed in compounded rubber but they can be attributed to other causes (vacuole formation) (*see* pages 415 and 432).

We are indebted to G. B. Deodhar[24] for more recent work relating elongation and Poisson's ratio, particularly in reference to the decrease with increasing elongation of the test piece. H. F. Schippel[25] and W. W. Vogt

[20] Among more recent determinations of Poisson's ratio should be mentioned the work of L. Bouchet, *Compt. rend.*, **158**, 1495 (1914). The value given there is 0.4998.

[21] *Compt. rend.*, **99**, 130 (1884).

[22] *J. Phys.*, [4], **2**, 490 (1903).

[23] In regard to the change in volume with elongation *see* p. 415 and p. 432.

[24] *Phil. Mag.*, [6], **45**, 471 (1923); also see Ono, *Math.-Phys. Soc. Tokyo*, [2], **7**, 36-43 (1913).

[25] *J. Ind. Eng. Chem.*, **12**, 33 (1920).

and R. D. Evans [26] investigated the dependence of the constants upon the form of the filler particles in pigmented vulcanized compounds, differentiating between anisotropic pigments* (such as graphite, mica, and magnesium carbonate) and isotropic pigments (such as carbon black, zinc oxide, and lithopone).[27] The isotropic fillers all gave values of $\mu' = 0.5$ for small elongations. These values, as well as the other properties of rigidity, appeared to be independent of whether the test piece was elongated in a direction perpendicular to or parallel to the calender grain for isotropic fillers.

The Work of Elongation. In considering the elastic deformation from an energy standpoint, the stored-up potential energy of the rubber can be considered as measured by the work which is done on the rubber to elongate it. As usual, it is given by the product of the force and elongation: $dA = pdl$; or integrating,

$$A = \int_{l_1}^{l_2} pdl \qquad (11)$$

The evaluation of this integral may be best accomplished graphically, by drawing the stress-elongation curve. Insofar as any permanent change in form results, the work of elongation is not completely transformed into potential energy since some of it is irreversibly utilized in producing the change in structure and some is dissipated in the form of heat. Aside from this, there has been some success in attempts to find an empirical formula by which the above integral could be solved algebraically. These analytical formulae will be considered later during the discussion of stress-strain curves. (*See* p. 404.) Their application, however, requires the determination of a large number of new constants in each particular case, so that in all practical cases the convenient graphical solution is given the preference.

While the investigations of elongation are concerned with elongations in one direction as a rule, M. Kröger [28] has studied the phenomenon of the stretching of rubber membranes. With these, the experimental evidence indicates that an entirely different type of energetic strain is encountered. By means of particularly ingenious apparatus, the curve showing the relation between the pressure and the displaced volume was obtained photographically. These curves may therefore be regarded as providing a measure of the work done to produce "lamellar packing." Raw rubber, synthetic rubber, and vulcanized "cut sheet" and compounded rubber were investigated at different temperatures. (*See also* p. 508.) In contrast with the linear tension, it was found that with increasing deformation, this bilateral tension passes through a maximum, then through a minimum, before reaching its final value. At the beginning of the swelling, the pressure increased rapidly and almost linearly. The mechanical work which can be stored in the rubber by such a strain appears to be 50 to 70 per cent less than that in the case of elongation (2 to 3 kg. m./cm.^{3} of rubber as compared to 6 kg. m./cm.^{3} for the usual tensile test). Deformation by elongation therefore permits a greater strain. It remains to be seen whether or not this conclusion is of general validity.

[26] *Ind. Eng. Chem.*, **15**, 1015 (1923).

* Translator's Note. For a definition of the word "pigment" as used throughout this section, *see* p. 374. N. J.

[27] It should be noted that the distinction between "isotropic" and "anisotropic" pigments does not refer at all to the distinction between amorphous and crystalline materials. The authors designate all pigments the outer form of whose particles shows no preferred axis as isotropic, because such pigment particles do not set themselves with a certain axis in the direction of the elongation when the compound is elongated.

[28] *Kolloid-Z.*, **45**, 52 (1928). Reference will be made to this work again in the discussion of double refraction and of the theory of pigment reinforcement.

Other Types of Strains. By using the modulus and Poisson's ratio as defined above, deformations such as bending, torsion,[29] etc., can be treated mathematically in a manner similar to that used for tensile deformations. The deformations which are produced by pressure are much less striking than those produced by tension. According to investigations by Stévart[30] on ring-shaped discs, the law of constant volume holds within certain limits here in the manner in which it would hold completely for fluids. The compressibility of the rubber is not inconsiderable at the beginning, when the width of the ring increases at the expense of its thickness. With increasing pressure the width of the ring increases more slowly. The experimental results can be represented by an empirical formula which depends largely on the shape of the test piece. Such results are of more interest to the technologist than to the physicist, especially when the elastic limit is exceeded considerably. Nevertheless, it is worthy of note that the course of the deformation produced by compression can be expressed satisfactorily by an equation.

In his work Stévart used ring-shaped cylindrical discs of various dimensions (*see* p. 554) made from a compound having a high rubber content and a specific gravity of about 1.06. These were subjected by a step-by-step loading to a high pressure. Letting H stand for the original thickness of the disc under no load, and h the momentary thickness under a loading of P in tons, Stévart finds the relationship

$$\frac{H}{h} = \frac{h}{H}aP + \frac{h}{H}$$

where a is a constant depending on the form of the test piece. Solving for $\frac{H}{h}$ he obtains

$$\frac{H}{h} = \sqrt{aP + 1} \tag{12}$$

For the constant a, Stévart found the expression

$$a = \frac{KH}{S}$$

in which S is the cross-sectional area of the test piece and K is a constant which is independent of the shape of the test piece, and is dependent only on the material of the test piece. Stévart's final form for the equation then becomes

$$\frac{H}{\sqrt{\frac{KHP}{S} + 1}} \tag{13}$$

For the compounds used by Stévart, K was equal to about 300. The value of K was found to be smaller when the rubber was more dense and less elastic. It is of interest to note that the volume of the rubber was not changed by compression in this manner but rather behaved exactly like a fluid in an elastic but resistant vessel. (*See* p. 432.)

[29] See J. Villey, P. Vernotte and F. Fontenay, *Compt. rend.*, **178**, 1418 (1924).

[30] *Bull. musée ind. Belg.*, **59**, 5 (1871); **63**, 5 (1873).

More recently R. Ariano [31] has investigated the same problem thoroughly. Cylinders of a vulcanized compound (100 parts of rubber and 8 parts of sulfur) were compressed to different degrees down to 45 per cent of their original height. A series of experiments showed that the behavior of the rubber conformed to equations quite well. Letting X stand for the force per unit original cross section, x the force per unit cross section referred to the momentary value, y the compression expressed as a fraction of the original height, and y' the ratio of the momentary diameter of the cylinder to the original diameter, the following equation, in which B and C are constants, was found to hold:

$$Xy + BX + Cy = O \tag{14}$$

For the compound mentioned above, $B = -0.95$ and $C = 113$. A technically cured compound (tire stock) behaved in a similar manner, but could be distinguished by a larger value for the constant C ($= 532$). B was found to depend only slightly on the nature of the compound and was generally approximately equal to —1. For the last mentioned compound B was found to be equal to —.99.

The equation

$$x = \left(\frac{C}{B}\right) y \tag{15}$$

holds for the relation between x and y, in agreement with experimental results. The equation corresponds to a tangent running through the origin of each hyperbolic curve.

Finally, the relationships between X and y' and between x and y' can be deduced in order to show how completely the compression phenomenon may be described by these formulae. These relationships are

$$(1 + y')^2 [C + (B + 1)X] = X + C \tag{16}$$

$$(1 + y')^2 \left(1 + \frac{BX}{C}\right) = 1 \tag{17}$$

The practical significance of these equations is not great, however, because their application requires the careful collection of a large amount of data in each individual case. Accordingly, they cannot be used, *a priori,* to describe the behavior under compression for any optional compound. However, it is of value to have these functions for use as interpolation formulae which may be applied to any portion of the compression test. Corresponding to Stévart's equation (13), Ariano introduces the ratio of momentary height to the original height into equation (14) and obtains the relationship

$$\frac{h}{H} = \frac{1}{\frac{X}{C} + 1} \tag{18}$$

In regard to the detailed proof and discussion of these equations the original paper must be consulted. It will be sufficient here to mention further only the equation for the work of compression, (*see* equation (11), p. 399).

[31] *Nuovo Cimento* (N. S.), **2**, 415 (1925); **4**, 263 (1927); **5**, 77 (1928); **6**, 123 (1929); also *India Rubber J.*, **72**, 271 (1926); **75**, 759 (1928); **76**, 207 (1928). It may be mentioned here that Ariano's concept of the Joule heat of elongation as being due to frictional heat cannot be maintained. (*Also see* p. 423 and p. 436.)

$$A = \int_H^h p \cdot dh$$

which may be expressed in the form

$$A = BC\left(\ln\frac{B+y}{B} - \frac{y}{B}\right) = BC\left(\ln\frac{C}{X+C} + \frac{X}{X+C}\right) \quad (1)$$

It should be noted that these equations hold even for strains so large that a permanent set occurs. A more thorough discussion of such strains will follow in the next section.

In connection with the compression of rubber, the recent work of C. H. Birkitt and T. J. Drakeley [32] should be mentioned. In this work the dependence of the compressibility upon the thickness of the test piece was investigated. Finally, P. W. Bridgman [33] has used rubber along with iron, phosphorus and paraffin in investigating the properties of matter under extremely high pressures. Rubber, in the form of a soft gum test piece, became as hard as steel when subjected to a pressure of 20,000 atmospheres.

An extensive investigation of the compression stress-strain relations in rubber was made by J. R. Sheppard and W. J. Clapson* [*Ind. Eng. Chem.*, **24,** 782 (1932); *Rubber Chem. Tech.*, **6,** 126 (1933)]. Compression strains as high as 97.4 per cent were reported, and compression stresses of 130,000 lbs. per sq. in. were applied. The method involved the inflation of balloons. (See p. 560 for further details.) It was found that the compression and extension curves are practically continuous through the stress-strain origin. Several methods of analysis of compression strain data are described.

Anisotropic Behavior. (Elongated Rubber.) If, at the beginning of an elastic test, the rubber is not an isotropic medium, the direction in which a force acts upon it will be of great importance in regard to the elastic reaction. Such a condition may exist when the rubber is already strongly stressed at the beginning of the test. Such behavior has been studied by Hock and Jentzsch.[34] They have studied the resiliency of elongated rubber strips by means of an apparatus in which a small steel ball fell from a certain height upon an inclined slab of elongated rubber. After the rebound, a measurable value of the throw was obtained, and the result was found to depend on the orientation of the elongated slab.

Partially Reversible Deformations (Hysteresis)

When rubber is strained beyond the elastic limit, the stress-strain relationships are not so easily discernible. However, in this region the conditions are comparable to those under which rubber may be used in actual service, and such deformations are therefore of considerable technical interest. In this region there is no longer any simple law for the dependence of the extension upon the force, but the form of the stress-strain curve is an important criterion for the technical properties of the rubber compound. For this reason, these questions merit a more thorough discussion in the treatment of the mechanical and technical tests. (*See* following section.) On the other hand, the physical changes which occur when rubber (especially unvulcanized rubber) is strongly extended have attracted the attention of physicists and have

[32] *Trans. Inst. Rubber Ind.*, **3,** 462 (1928).

[33] *Eng. Mining J.*, **112,** 535 (1921).

* Translator's note by N. J.

[34] *Z. Elektrochem.*, Bunsenvortrag. **31,** 404 (1925). In reference to this method of investigation, the work is considered more in detail in the following section (*see* p. 569).

given rise to many investigations. Because of the connection of this subject with the important question of the elastic nature of rubber, consideration is now to be given to this domain in which Hooke's law no longer holds. Within this region strictly elastic phenomena are no longer to be found. A certain part of the energy applied to produce deformation is used in producing a change in state which manifests itself as elastic hysteresis, while another portion is without doubt transformed into heat. Therefore, only a fraction of the applied energy reappears as external work. The extension, from the beginning to the end which is reached when the test piece breaks, has been described by equations set up by various authors. These equations contain several constants and are similar to those presented during the discussion of compression. (*See* p. 401.)

Cheneveau and Heim [35] were the first to attempt to set up a suitable interpolation formula:

$$y = cx + a \sin^2 bx \qquad (20)$$

(Ordinate y = elongation in cm.; abscissa x = force in kg.; and a, b, c = constants.) If l and q stand for the length and the cross section of the test piece, and k and α for constants dependent on the nature of the rubber, c and a are given by the equations

$$c = k\frac{l}{q}$$

and

$$a = \alpha\frac{l}{q}$$

For unit length and cross section, equation (20) becomes

$$y = kx + \alpha \sin^2 bx$$

The constant b is independent of the dimensions of the test piece and does not express the technical quality of the rubber to the same extent as k and α. Constants a, b and c are characteristic of the extension in the middle, last, and first parts of the tension test, which fact has led the authors to connect them with certain changes in the individual rubber particles. (*See* p. 417.) The equation has been developed further by Hatschek and Goldsbrough [36] and by Schidrowitz,[37] and has been discussed particularly from a technical viewpoint. This matter will be considered again in connection with the discussion of the idea of "slope" (*see* p. 521).

Recently Ariano has successfully developed an analytical expression for the stress-strain curve. From his fundamental equations, he deduces Poisson's ratio both for extension and for compression phenomena. The stress-strain curve is represented by an equation corresponding to equation (14) (*see* p. 401):

$$xy + bx + cy = 0 \qquad (21)$$

where x stands for the force in g./mm.^{2} referred to the momentary cross section of the extended test piece and y for the elongation. For a compound containing 100 parts of rubber and 8 parts of sulfur, vulcanized for 40 min-

[35] *Compt. rend.*, **152**, 320-322 (1911).

[36] *J. Soc. Chem. Ind.*, **38**, 347T (1919). Emil Hatschek has given a further discussion of the mathematical form of the stress-strain curve in *J. Soc. Chem. Ind.*, **40**, 251-253T (1921). Compare also W. B. Wiegand, *India Rubber J.*, **60**, 379-383, 423-429 (1920), and O. de Vries, *J. Soc. Chem. Ind.*, **39**, 308-310T (1920) where the development by Schidrowitz is criticized.

[37] *J. Soc. Chem. Ind.*, **38**, 348T (1919).

utes at 123° C., Ariano obtained the following illustrative values: $b = -10.33$; $C = 854$. If X is the stress in g./mm.^{2} referred to the original cross section, and if it is assumed that the volume is constant (*see* pages 398 and 401), then

$$x = X\ (y + 1) \tag{21a}$$

and equation (21) becomes

$$Xy\ (y + 1) + bX\ (y + 1) + cy = 0$$

From this fundamental equation Ariano obtains comparatively simple expressions both for Young's modulus of elasticity E and for Poisson's ratio μ':

$$E = \frac{-(x + c)^2}{bc}; \qquad \mu' = \frac{b'c}{y\ (c' - c) + bc'} \tag{22}$$

In the last equation use is made of the constants b' and c' which result from b and c of equation (21) when y stands for the transverse contraction. Illustrative values of these constants are $b' = -0.685$; $c' = 119.78$. For the compound mentioned above in the case of minimum loading ($x = 0$), $\mu' = 0.473$. At the highest elongation reached ($y = 10.33$), μ' had decreased to the value 0.066. (*See* p. 398.) The work of extension may be deduced from equation (21) by integration. The resulting formula corresponds to equation (11) which held for compression.

$$A = \int_o^y x \cdot dy = bc\left(\log \frac{b + y}{b} - \frac{y}{b}\right) \tag{23}$$

As has already been emphasized, this work of extension is not all reversibly stored up as potential energy when the elongation is large; only a part of it is available again. The difference represents the hysteresis loss, which is always to be observed in cycles of loading and unloading. (*See* the following paragraph.)

The hysteresis loss in a compression cycle applied to rubber in the shape of a balloon has been fully discussed by J. R. Sheppard and W. J. Clapson* [*Ind. Eng. Chem.*, **24**, 782 (1932); *Rubber Chem. Tech.*, **6**, 126 (1933)]. Hysteresis losses were of the order of 29 to 35 per cent of the work of compression, when the strain was near rupture.

Stress-Strain Curves for Loading and Unloading. If the curve of a loading and unloading cycle be plotted on a stress-strain diagram, the points representing pairs of values of stress and strain for retraction will not fall on the same curve as those for extension. Instead, the elongation corresponding to any loading will be greater on the retraction curve than it was on the elongation curve. This is true even when the load is reduced to zero, since a permanent deformation remains. Accordingly, we speak of an elastic after-effect and of elastic hysteresis, and consider this phenomenon to be analogous to the phenomenon of residual magnetism found in the magnetization and demagnetization of iron. In Figures 59 and 60 are shown typical illustrations of the course of such cycles. The first figure shows the behavior of a test ring stamped out of a smooth slab of crude sheet. The ring, which weighed 1.5 g., was of the usual dimensions for testing purposes, and was slowly elongated on a Schopper dynamometer. The ordinates represent the values of the acting force in kilograms. Both the distance of travel of the drawbar in meters and the amount of elongation (in per cent) of the original inner circumference of the ring (14 cm.) are marked on the ab-

* Translator's note by N. J.

scissa.[38] The large hysteresis loop was obtained from the first cycle of elongation of the ring and the smaller loop from the second cycle, taken immediately afterward, using the same ring. The measurements were made at room temperature, with a drawbar velocity of 12 cm. per minute. These specifications are included in order to emphasize the fact that the stress-strain relation is very greatly dependent on the time and temperature, and is characteristic of the test piece only at the particular instant when determined. Measurements made after an interval of several months, for example, might yield considerably different results.[39] In regard to these considerations, crude rubber is much more sensitive than vulcanized rubber. Turning again

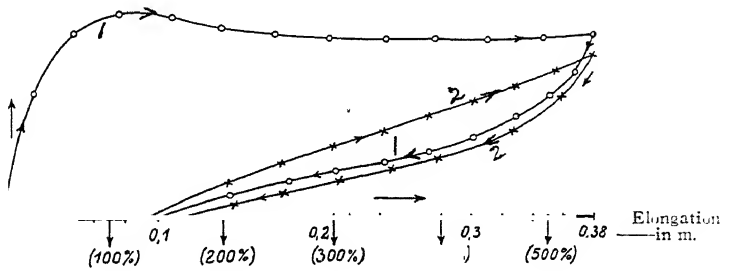


Figure 59—(Above)—Hysteresis curves:

Curve 1: Typical first extension and contraction curve for raw rubber.

Curve 2: Typical second extension and contraction curve for raw rubber.

(According to L. Hock and S. Bostroem.)

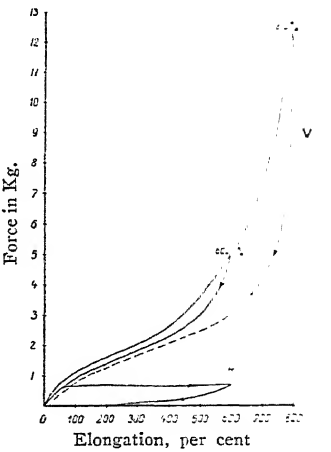


Figure 60—(Right)—Hysteresis loops with reversal at 600% and 800% extension, for 1.5 grams of vulcanized rubber (V), and with the reversal at 600% for 1.5 grams of raw rubber (R).

(According to L. Hock and S. Bostroem.)

to the figure where the directions in which the curves were run are shown by arrows, we see that the required force increased rapidly up to an elongation of about 100 per cent, while for further elongation the force remains practically constant. At that point there appears a flow phenomenon, which is characterized by the fact that the overcoming of a practically constant resistance permits of further elongation. According to the molecular concept, it may be supposed that what is taking place is merely a rearrangement of the molecules or micelles of which the rubber is built up. Also we here find support for the supposition that in this stage of the elongation process, an

[38] See also the discussions by L. Hock [*Kautschuk*, **3**, 314 (1927)] concerning the planimetric determination of the work of elongation and concerning the connection between the ring dimension and the motion of the drawbar. *See also* p. 500.

[39] For example, see S. Bostroem, *Kolloidchem. Beihefte*, **26**, 465 (1928).

alignment of the molecules takes place, assuming that they are oblong in shape.[40]

A considerable permanent set remains after the complete relaxation of the tension, and the second cycle is begun at that point. The percentage elongation is again calculated on the basis of the original inner circumference of the ring. The shape of the second curve is entirely different from that of the first. Beginning with a small value, the force increases constantly until the point of reversal is reached. After the reversal, the retraction curve returns very closely underneath the retraction curve of the first cycle. If the experiment be repeated, the hysteresis loops for subsequent cycles will coincide closely with the second cycle and with one another.

Figure 60 shows a hysteresis loop for a similar ring of vulcanized rubber which was prepared from the same crude rubber by the use of sulfur (6 per cent) and Vulkacit (1 per cent). For comparison, the curve of Figure 59 (*R*) is given again. It can be seen that the curve (*V*) for the vulcanized rubber lies high above that for the crude rubber. The same curve represents two experiments. The maximum elongation of the first cycle was 600 per cent, as in the case of the crude rubber. The elongation for the second cycle, for which the retraction curve is broken, reached a value of 800 per cent. For any given elongation, the mechanical work performed in stretching the ring, which is expressed by equation (11), is given by the area inclosed between the curve and the elongation axis. By comparing the areas of the hysteresis loops we can see how much energy loss results from hysteresis for any cycle. This energy loss represents work done in heating and in permanently changing the form of the ring. At 600 per cent elongation, the areas of the hysteresis loops for crude rubber and vulcanized rubber are approximately the same, in spite of the fact that the work of elongation for crude rubber is only about one-fourth as much as that for vulcanized rubber. The vulcanized rubber, therefore, shows a proportionately smaller energy loss, which is accompanied by a smaller permanent set, as can be read off on the elongation axis. Also, in more highly vulcanized rubber there is less difference between the first loop and subsequent loops, which are not shown on the figure. A further discussion of these curves and a comparison of the amount of work involved in the different cases will be presented later. However, we may note here that the capacity of the rubber for storing up mechanical work is increased to an extraordinary degree by vulcanization. This is particularly evident from comparisons of samples of the same compound.[41] (*See also* p. 500.)

The stress-strain curve for soft rubber, such as the typical curve shown in Figure 60, may be contrasted with such a curve for steel or iron. It will be seen that, along with the great difference between the moduli of elasticity of the two, the elongation of the metal will be small for small stresses until the elastic limit is reached, after which the elongation will increase more rapidly than the stress. This effect is even more evident at still higher elongations

[40] See L. Schiller, Dissertation, Leipzig, **1911** (*see also* p. 418 of this book). In addition: L. Hock, *Kolloid-Z.*, **35**, 40 (1924). The work of H. Lorenz, "Verhalten fester Körper im Fliessbereich" (Leipzig, **1922**), in reference to flow phenomena in general should also be mentioned here.

[41] The dependence of the nature of the stress-strain upon the degree of vulcanization can be used as a criterion for the technical determination of the optimum cure; see for example R. P. Dinsmore and A. O. Zimmerman, *India Rubber J.*, **72**, 187 (1926), H. P. Gurney and C. H. Tavener, *J. Ind. Eng. Chem.*, **14**, 134-139 (1922), as well as H. P. Gurney, *ibid.*, **13**, 707 (1921). These authors investigated—from a technical point of view—the capacity of vulcanized compounds for storing energy (hysteresis, etc.). Para rubber and plantation rubber were compared, and the influence of the previous treatment of the crude rubber was studied.

when the yield point is reached. Rubber behaves in a manner which is exactly opposite; in the region of low tension a large elongation corresponds to a given stress increment, but when higher stresses are reached the corresponding increment in length is much less, until at last the stress-strain curve runs almost parallel to the stress axis. Therefore in the region of tension which just precedes rupture, the rubber experiences almost no elongation. This behavior gives the twice bent, S-shaped curve which is typical of soft rubber compounds.[42]

Observations on the elastic after-effect have been made by investigators who have been concerned with the determination of the constants of rubber. A thorough investigation by Hesehus [43] has led to the conclusion that, for deformations of short duration—provided they are not excessively large—the elastic after-effect is vanishingly small. Even if the rubber has not previously been stressed, it returns quickly to the equilibrium condition as if it had been previously stressed. The greater the surface for a given mass, the less prominent is the elastic after-effect. The after-effect can also be reduced by increasing the temperature.

At about the same time, Bouasse [44] also investigated the elastic after-effect. He studied particularly the results of successively repeated loadings. A. Schwartz [45] has conducted a very commendable systematic series of experiments in regard to the same subject.[46]

Phillips [47] has investigated the important influence of time. He observed the increase in elongation under a constant load, and the dependence of the elastic after-effect upon the time which elapsed after the load was applied and after it was removed. He obtained thereby a logarithmic function of the time

$$x = b \log \frac{t}{t_0} \qquad (24)$$

where x stands for the residual elongation, t the time elapsed after loading, and t_0 the time elapsed after unloading. The constant b is dependent upon the rubber being tested.

The Effect of Temperature on the Stress-Strain Curve. Since the elastic after-effect and the occurrence of hysteresis loss are of outstanding significance for the technical evaluation of rubber compounds, the methods of their measurement belong in the domain of rubber testing. However, some of the general facts will be discussed here. In this connection J. C. Shedd and Ingersoll [48] have thoroughly investigated the elastic hysteresis and the influence of heat upon it. The tests were made on strips of rubber which were loaded either by means of a scale pan and shot or by water. The load was changed by steps which were separated in time by hours or days, while at the same time the corresponding changes in elongation were determined by means of a cathetometer. In this manner they obtained hysteresis loops such

[42] An interesting technical comparison of vulcanized rubber with steel in regard to mechanical performance has been made by W. A. Gibbons, *India Rubber World*, **75**, 317 (1927). In analogy to the theory of "corresponding states," metals should properly be compared with rubber only when the latter is at very low temperatures. It should prove very fruitful indeed to make the comparison under those conditions. (See Pólányi and Schob, p. 431.) E. Hungerer and J. Koenigsberger [*Z. Physik*, **31**, 903 (1925)] refer to rubber, which is strictly elastic in regard to small deformations, as a substance without noticeable plasticity, in contrast to materials such as metals (or waxes and rosin), which can be plastically deformed.

[43] *J. Russ. Phys. Chem. Soc.*, **14**, 320-385 (1882); *Beibl. Ann. Physik*, **7**, 654 (1883).

[44] *Ann. Sci. Toulouse* [2], **6**, 177 (1904).

[45] *J. Inst. Elec. Eng.*, **44**, 693 (1910); *India Rubber J.*, **39**, 104, 147, 278, 341, 410 (1910).

[46] Information about additional investigations is given by G. S. Whitby, "Plantation Rubber and the Testing of Rubber," Longmans, Green & Co., London, **1920**.

[47] *Phil. Mag.* [6], **9**, 513 (1905).

[48] *Phys. Rev.*, **19**, 107 (1904).

as have already been described at temperatures between 11° and 93° C. These curves show that the hysteresis loss decreases rapidly with increasing temperatures, and asymptotically approaches a certain limiting value. Figures 61 to 68 show the hysteresis curves obtained by Shedd and Ingersoll for a given compound at various temperatures lying between 11° and 93° C. These curves also show the influence of temperature on the stress-strain curve, a discussion of which will be presented later, in another connection (*see* p. 519). It should be particularly noticed that in these investigations also, the energy taken up by rubber becomes less with increasing temperature, so that not only the absolute size of the hysteresis loss should be considered, but also its size in relation to the total energy absorbed in the elongation. Along this line, Hock and Bostroem [49] have determined the absolute and the relative magnitudes of the hysteresis loss both for single and repeated cycles, using rings from unvulcanized sheets. They expressed the hysteresis loss in physical units of work (kilogram-meters and calories). The determination of the work of elongation for the same material at higher temperatures gave definitely smaller values.[50] As in the experiments of Shedd and Ingersoll, the strong negative temperature coefficient of this work of elongation is outstandingly noticeable, and is to be attributed to the rapid decrease of the inner friction as the temperature is raised. That part of the work of elongation which is stored up as reversible potential energy, as will be pointed out later, should show a weak† positive temperature coefficient. Such work must, therefore, have a negligible influence upon the temperature function now under consideration. (*See* p. 439.)

A very thorough study of the physical-mechanical properties of vulcanized rubber at high temperatures has been made by A. van Rossem and H. van der Meyden.[51] These studies are not only of significance in regard to technical testing, but they also throw light upon the problem of vulcanization and reclaiming. Similar experiments have also been made by A. A. Somerville and W. H. Cope.[52] In addition to these, R. F. Tener, S. S. Kingsbury and W. L. Holt [53] have obtained tension curves for six different soft vulcanized compounds over a temperature range extending from −70° to +147° C., thereby extending the temperature range to lower temperatures. Especial mention must be accorded the conclusive investigation of M. LeBlanc and M. Kröger,[54] which has yielded valuable data with regard to the investigation of rubber structure. (*See* p. 427.) They have obtained elongation curves, together with data on permanent set, both for raw rubber and for compounds which were vulcanized to various degrees. At the same time the measurements were extended to low temperatures.

The Theory of Mechanical Disintegration. If, in addition to the work utilized in producing a permanent change of form, a further considerable

† Translator's Note. The translators point out that this statement is insufficiently qualified to be of general application. In Figures 61 to 68 the temperature coefficient of the work of elongation may be either positive or negative depending on whether the elongations are carried to constant maximum stress or constant strain. Its sign may be reversed, depending on the extent of the elongation considered, and on the temperature range considered. In the German edition, the stress-strain axes were incorrectly labelled, thus contributing to a confused interpretation. The common interpretation of more recent data is that the thermal coefficient is negative for elongations to constant strain, and positive for elongations to constant stress. At high temperatures, rubber exhibits its maximum tensile properties at shorter cures than at room temperature. A high rate of tensile testing increases the tensile properties in the higher temperature tests.—N. J.

[49] *Kautschuk*, **2**, 130 (1926).

[50] S. Bostroem, Dissertation, Giessen (1927). See also *Kolloidchem. Beihefte*, **26**, 439 (1928).

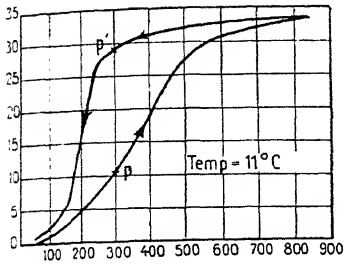
† See previous Translator's Note.

[51] *Kolloid-Z.*, **39**, 69 (1926); also Kautschuk, **3**, 364 (1927).

[52] *Trans. Inst. Rubber Ind.*, **4**, 263 (1928) and *India Rubber World*, **79**, 64 (Nov., 1928).

[53] *Bur. Stand. Tech. Paper*, **No. 364** (1928).

[54] *Kolloid-Z.*, **37**, 205 (1925).



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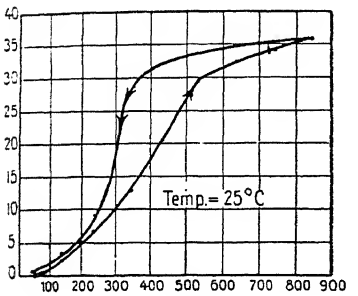

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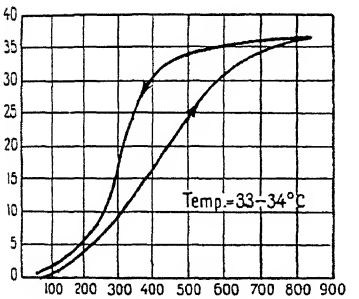

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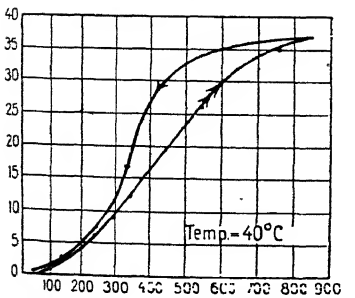

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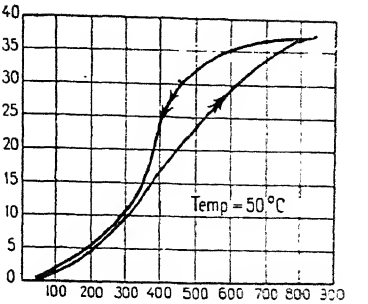

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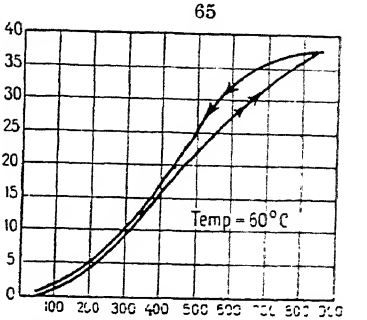
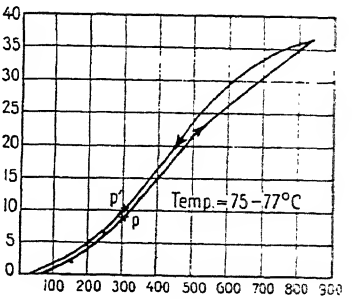


66

Elongation in cm. ↑

Load in grams →



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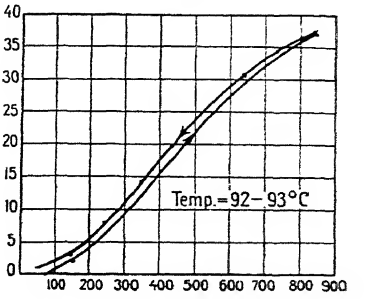

68

Figures 61-68—Dependence of the elastic hysteresis on temperature, determined on vulcanized compounds.
(According to Shedd and Ingersoll.)

portion of the work of elongation is transformed irreversibly into heat by friction, the heat so generated will result in a marked rise in temperature of the rubber when it is subjected to repeated periodic strains. The amount of the heat so generated will be greater the greater the hysteresis loss of the compound in proportion to the work of deformation and will also depend upon the absolute magnitude of the hysteresis loss. Hock [55] has developed a qualitative formula which expresses the resistance of a compound to mechanical disintegration in terms of its work of elongation and its hysteresis loss. This expression predicts the amount of internal heat which will be generated and which will tend to bring about a chemical decomposition of the rubber substance.

Resiliency.[56] An extremely quick method of determining the hysteresis loss for impacts may be made by means of the elastic rebound. This elastic rebound may be simply measured by the relative height H' to which a steel ball will bounce after falling on a rubber slab from a height H. The relative hysteresis loss will then be $\frac{H-H'}{H}$. Various methods of measuring this elastic rebound have been developed by P. Breuil [57] (Elastometer), A. Schob [58] (Pendulum Hammer) and L. Hock [59] ("Falling Ball" [Kugelweitwurfapparat]). Fol [60] determined the relation between elastic rebound and temperature by means of the elastometer. These results, as well as others obtained by Schob using the pendulum hammer, were in agreement with the above conclusion that an increase in temperature resulted in a considerable decrease in the relative hysteresis loss, which decrease must be ascribed to the decrease of inner friction.[61]

Rate of Elongation and Hysteresis. K. Memmler and A. Schob [62] have made a systematic study of the influence of the time element in loading upon the tensile strength and the stress-strain curve and have also studied the phenomena of the elastic after-effect after the load was removed. Since these investigations are of importance in the criticism of technical methods of testing, they will be treated more thoroughly in another place. Suffice it here to state that with each change in the method of straining the rubber there was a change in the amount of hysteresis. H. Feuchter [63] was able to show that raw rubber exhibited a large permanent set (50 per cent) when the elongation and retraction took place rather slowly. When the rubber was stretched out quickly to about 500 or 600 per cent elongation and allowed to snap back immediately, there was a permanent set of only about 2 per cent. When the strip (2x2x20 mm.) was kept in the elongated state for 3 seconds, a permanent "racking" of 500 per cent remained. A further consideration of the peculiar elastic behavior of raw rubber will be presented later. The last particularly striking example was given in this connection merely to show that the course of the stress-strain curve and the magnitude of the after-effect depend not only upon the change in length, but also upon the manner in which this change in length is produced. (*See also* p. 432.)

[55] *Kautschuk*, **1**, 14 (Sept., 1925). In regard to the technique of such tests, see p. 589 of this book.
[56] *Rückprallelastizität.*
[57] *Caoutchouc & gutta-percha*, **5**, 2186 (1908).
[58] *Gummi-Ztg.*, **34**, 995 (1920); see also p. 571 of this book.
[59] *Z. tech. Physik*, **6**, 50 (1925); *Kautschuk*, **1**, 19 (Sept., 1925).
[60] *Cf.* van Rossem, *Kolloidchem. Beihefte*, **12**, 171 (1920).
[61] A thorough analysis of impact phenomena (duration of impact, duration of effective contact, phases of impact, dynamic hardness) for both hard and soft rubber is given by G. Moreau, *Ann. phys.*, **14**, 306-333 (1920). See also L. Hock, *loc. cit.*
[62] *Mitt. Materialprüfungsamt, Berlin-Dahlem*, 4 (1909); see also the more complete treatment on p. 404 of this book, as well as the section on "Physical Testing Methods." P. Breuil has also investigated this question: see *Caoutchouc & gutta-percha*, **1**, 100, 122 (1904).
[63] *Kautschuk*, **3**, 149 (1927); **4**, 8 (1928).

The constants may be grouped together under the terminology used by Karrer [*Ind. Eng. Chem.*, **21**, 770 (1929)] and may be classified as elastic constants, pseudo-plastic and plastic constants. The elastic behavior of a rubber may be completely defined by these five constants. The reader is referred to the original work for mathematical details.

The influences of temperature and of the rate of elongation upon the stress-strain curve of raw rubber are shown in Figures 69 and 70, which show some of the results obtained by E. A. Hauser, P. Rosbaud and E. Schmid [64] in an investigation of this question. (*Compare also* Fig. 77, p. 441.)

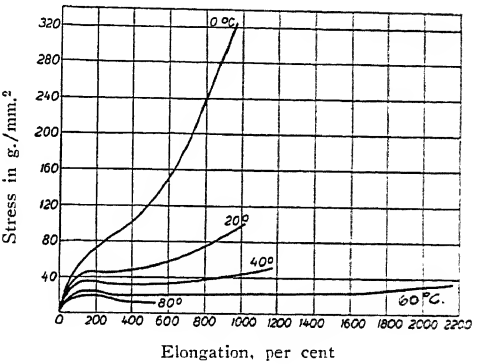

Figure 69—Stress-strain curves at various temperatures.
(According to E. A. Hauser, P. Rosbaud and E. Schmid.)
(Stress calculated on original section.)

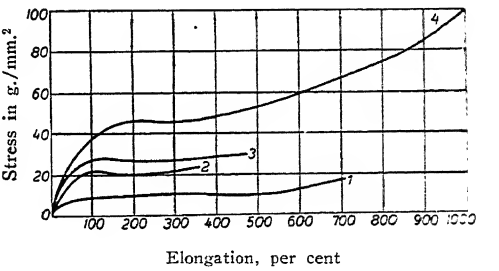

Figure 70—Stress-strain curves for various rates of extension.
(According to E. A. Hauser, P. Rosbaud and E. Schmid.)
(Stress calculated on original section.)
Curve 2 taken at about 0.025%/sec.
Curve 3 taken at about 0.1%/sec.
Curve 4 taken at about 3.0%/sec.

Finally, in this connection should be noted briefly the work of O. deVries and H. I. Hellendoorn.[65] These investigators studied the relation between the degree of vulcanization and the permanent set, which decreases as the degree of vulcanization increases. (*See* p. 606.) The study of F. W. G. King and A. G. Cogswell [66] in regard to the action of continuous forces on rubber should also be mentioned. The influence of the degree of vulcanization is also treated in the above-mentioned work of LeBlanc and Kröger.

The effect of compounding or reinforcement of the rubber upon the hysteresis losses has been studied by H. Barron and F. H. Cotton* [*Trans. Inst. Rubber Ind.*, **7**, 209 (1931); *Rubber Chem. Tech.*, **5**, 336 (1932)]. They found the following results:

"1. The hysteresis loss in vulcanized rubber during a cycle of extension and retraction increases with amplitude to an extent comparable with the increase in the work of extension.

[64] *Kautschuk*, **4**, 12 (1928); also *Z. tech. Physik*, **9**, 98 (1928). A space model of the elongation-flow curve is given there, as well as the experimental details.

[65] *J. Soc. Chem. Ind.*, **36**, 1258-1262 (1917).

[66] *India Rubber J.*, **63**, 30-32 (1922).

* Translator's note by N. J.

"2. If the work required to extend a vulcanized rubber to a given elongation be increased by compounding with fillers, the energy lost through hysteresis on slow retraction increases to a comparable extent. Hence reinforcement does not appreciably increase the ability of rubber to store energy.
"3. With any rubber vulcanized to optimum tensile properties, hysteresis loss and work of retraction from any elongation are proportional to the work required to extend to that elongation. Therefore, if the hysteresis loss during a given cycle be known, the work of retraction from the breaking point can be calculated.
"4. The work of retraction of the ultimate breaking point of a vulcanized rubber increases slightly with reinforcement, and becomes greatest when the reinforcement is at a maximum. This is thought to be a function of the rubber-filler interface.
"5. No filler was found to lessen the work of retraction from the breaking point until the rubber was highly compounded.
"6. It is suggested that the increased work required to rupture rubber that has been reinforced with fillers is mainly dissipated in overcoming consequent increased internal friction, a small quantity being converted to potential energy through strain of the rubber-filler interface."

A comparison between the physical properties of rubber and balata is given by the stress-strain curves obtained by C. R. Park.[67] Balata, when loaded, elongates in a manner similar to a metal. A mixture of rubber and balata shows the properties of a transition material. It can be said that high temperature makes the balata behave like rubber, while low temperature makes the rubber behave like balata.

The Physical Structure of Rubber as the Cause of Its Peculiar Thermal and Elastic Properties (The Gough-Joule Effect)

Summary of Phenomena Connected with the Gough-Joule Effect

Thomson's Theoretical Suggestion. The discovery of William Thomson (Lord Kelvin) [68] that a rubber strip will become heated when elongated quickly to a considerable degree, marks the beginning of a fruitful series of investigations of the unusual thermal and elastic behavior of rubber. This behavior, which is the opposite of the behavior of metals in this respect, led to the conclusion that an elongated rubber strip must become shorter when heated, according to a thermodynamic principle which had already been pointed out by Thomson. From the two fundamental laws of thermodynamics, it follows that a stretched wire must shorten when heated if the process of elongation produces heat, and it must lengthen when heated if the elongation absorbs heat. These laws also follow directly from Le Chatelier's law.

Joule's Experiment. The prediction of Thomson was experimentally verified by Joule,[69] who used a rubber tube elongated by weights to three times its normal length. When the tube was warmed by the heated air from an alcohol flame it became noticeably shorter. This experiment can easily be repeated by passing a stream of hot air or steam through an elongated tube. The shortening can be made easily visible by means of a lever with a pointer and scale.

[67] *Ind. Eng. Chem.*, **17**, 152 (1925).

[68] See J. P. Joule, *Trans. Roy. Soc.* (*London*), **149**, 91 (1859). In this classic work is found reference to the priority of John Gough, who was the first to study the peculiar behavior of rubber. (*See* p. 404.)

[69] This experiment is described more in detail in the book, "Heat," by J. Tyndall; (German translation, "Die Wärme," by Helmholtz and Wiedemann, p. 114, **1871**).
The experiment had already been performed by J. Gough (1805), using raw rubber (see p. 415).

Wiegand's Pendulum. W. B. Wiegand [70] has recently demonstrated the Joule-Thomson effect, in a particularly clear and convincing manner. He utilized the contraction of the rubber to make a periodically-acting heat engine, in which the substance which performs the work is a thin strip of vulcanized rubber instead of water or an explosive gas mixture. Assuming complete reversibility of the elongation process and of the thermal manifestations connected with it, the rubber band can be carried through a cyclic process analogous to a Carnot cycle.[71] The assumption of complete reversibility is of course fulfilled in rubber only to a certain practical extent. The rubber in an elongated state increases in temperature by absorbing a quantity of heat, thereby contracting and performing work. The rubber is then brought to a lower temperature and maintained at that temperature while being elongated by means of work done on it from without. The heat given off by the rubber during elongation is absorbed by the surroundings. If this elongation be just enough to bring the rubber back to its original elongation, the cycle will be completed by bringing the rubber up to its original temperature. If the rubber is enabled to perform work by taking up a quantity of heat Q at a high temperature T_1, the fractional part of that heat which can be transformed into work will be $\frac{T_1-T_2}{T_1}$, where T_2 is the lower temperature, provided the assumption of the reversibility of the elongation process is correct.

According to this fundamental principle, Wiegand constructed his periodically-acting machine, which is illustrated in Figure 71. This machine consists essentially of a pendulum formed by a long iron rod attached to a knife edge and hanging from a bearing attached to a support. Above and below the knife edge A are sliding weights P, which may be clamped at any point along the bar, and which are so adjusted that the assembly swings as a pendulum to the right or left in a fixed plane. One end of a rubber band K (110x 30x0.5 mm., for example) is fastened in a clamp which is in turn attached to

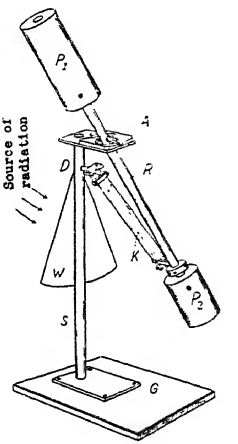

Figure 71—"Rubber Pendulum." (Joule experiment.) (According to W. B. Wiegand.)

[70] *Trans. Inst. Rubber Ind.*, **1**, 141 (1925); see also *India Rubber World*, **73**, 200 (1926).

[71] See, for example, a textbook of physics, or John Eggert, "Lehrbuch der Physikalischen Chemie auf elementarer Grundlage," edited by L. Hock, 2nd ed., p. 40, S. Hirzel, Leipzig, **1929**. English translation, "Physical Chemistry," by S. J. Gregg, Van Nostrand, New York, **1933**.

a rod on the support just underneath the knife edge, while the other end of the band is fastened in a clamp which is hooked to an eye on the pendulum rod. When the pendulum swings out, the rubber band, which is under an elongation of 100 to 200 per cent, is subjected to an added tension. The rubber is then at the starting point of the theoretical cycle described above (the point at which the addition of heat will bring about a contraction). The radiation from an electrically heated resistance unit furnishes this heat to the band, which is intentionally blackened. The pendulum immediately swings back to the center under the force of contraction of the rubber band, and as it swings on over to the other side it again puts the rubber under tension. Here the radiation again strikes the rubber and the pendulum swings back into its first position again; and so on. It is advantageous to enhance the action of the device by directing a stream of cold air against the rubber band during that part of the period when the band is being elongated. When this unusual heat engine is used to illustrate the theory of cyclic processes—a use for which it is recommended—the cold blast furnishes an obvious example of a heat sink at the lower temperature. In the same article, Wiegand describes another periodically-acting heat engine, consisting of a wheel which is caused to rotate about an eccentric axis by the action of a source of heat. Both of these devices are based upon the fundamental Gough-Joule effect.

Both the pendulum and wheel mechanisms for the demonstration of the Gough-Joule effect are quite reliable mechanisms for such a demonstration.* One model of each type operated continuously for 150 days at the Chicago Exposition ("A Century of Progress Exposition") during the summer of 1933, with only occasional attention. In a personal interview with the translator early in 1933, Mr. Wiegand described three other types of heat engine involving the Gough-Joule effect in rubber. There were described two variations of the pendulum mechanism. Both of these involved a mass suspended by the rubber element, rather than by a rigid bar or rod. In one, heat was applied to the suspending rubber strip at each end of its swing, so as to increase the potential energy of the mass for the start of the reverse swing. In the other, heat was applied at the center of the swing, to shorten the effective radius of the pendulum at the point of maximum kinetic energy, thus increasing the potential energy. The third mechanism was essentially a rubber refrigerating element, which was subjected to the following cycle: (1) elongation; (2) cooling to room temperature; (3) introduction into insulated refrigeration chamber, with simultaneous retraction, which causes cooling; and (4) removal from refrigeration chamber preparatory to next elongation. A rubber band could be subjected to such a cycle of operations in a continuous manner, for demonstration of the Gough-Joule effect.

Joule's Measurements. Joule was the first to make a careful measurement of the heating produced by elongation (which corresponds to the cooling caused by contraction). Measurements were made on both crude and vulcanized rubber, the results for the former being given in Table 3.

The rubber strips were loaded step by step by weights placed on a suspended scale pan, and the corresponding elongation noted. The momentary changes in temperature which accompanied the additions of weight were determined by means of a sensitive thermocouple, the junction of which was held in contact with the rubber strip. By removing the weights from time to time, Joule observed the considerable permanent set which existed. He considered this to be so disturbing to his experiment that he (unfortunately) turned to the study of vulcanized rubber exclusively, since it behaved in a practically reversible manner. It should be noted that in the first stage of elongation, an appreciable cooling was found, which was immediately followed by an increasing heating effect. In Table 4 are shown the corresponding results obtained by Joule when using vulcanized rubber.

* Translator's note by N. J.

TABLE 3.—*The Heating of Crude Rubber as a Consequence of Elongation (Work of Joule).*

Load applied Pounds	Length of the rubber in inches Under the influence of the load	After the removal of the load	Change in temperature ° C.
—	0.59	0.59	—
2	0.67	—	—
4	0.77	—	—0.002
6	0.94	—	+0.020
8	1.13	—	+0.059
10	1.45	0.71	+0.139
12	1.75	0.90	+0.370
14	—	—	+0.537
16	2.14	—	+0.657
18	2.36	1.02	+0.750

TABLE 4.—*The Heating of Vulcanized Rubber as a Consequence of Elongation (Work of Joule).*

Load applied Pounds	Length of the rubber Inches	Change in temperature ° C.
—	4.00	—
2	4.06	—0.003
4	4.17	—0.004
7	4.30	—0.004
14	4.80	—0.001
21	5.21	+0.014
28	5.87	+0.053
35	6.60	+0.095
42	7.25	+0.137
49	7.75	+0.180

J. Gough as the First Observer of the Gough-Joule Effect in Rubber. It is of historical interest to note that J. Gough [72] had previously observed the peculiar elastic properties of rubber and that the priority in the discovery of the thermal effect in rubber should rightly be attributed to him, especially since he studied the phenomenon rather carefully. His observations have simply remained unnoticed, while those of Joule have become widely known. Joule states that he did not become aware of the work of Gough until after his own similar experiments with vulcanized rubber had been completed. As early as 1805 Gough had determined, by touching crude rubber strips to his lips, that the rubber was heated by stretching and cooled by contraction. A strip of crude rubber elongated by a weight was found to shorten itself when heated, and to lengthen again when cooled. If elongated while immersed in cold water, the rubber retained its elongation until the strip was warmed, when it again contracted. Gough was also right in one observation concerning which Joule disagreed with him; i.e., the density of rubber increased when elongated. If this disagreement does not result from a difference in the reliability of the experiments it might be cleared up by the fact that Gough experimented with crude rubber while Joule used vulcanized rubber. Furthermore, Joule determined the density of a sample elongated by only 100 per cent, in which case the effect would not be very noticeable. In addition, compounded rubber often actually does show an appreciable decrease in density on elongation. Schippel [73] concluded, after a systematic investigation, that this decrease in density was due to the formation of small vacuoles between

[72] J. Gough, *Memoirs of the Lit. and Phil. Soc. of Manchester*, 2nd series, **1**, 288 (1805). The present writer considers himself justified in emphasizing the part which Gough had in the discovery of the effect by calling it the Gough-Joule effect. The so-called Joule experiment was really first performed by Gough.

[73] *J. Ind. Eng. Chem.*, **12**, 33 (1920).

the rubber and the filler or pigment particles. The existence of these vacuoles was microscopically verified by Green.[74] That the rubber itself becomes more dense on being stretched has been demonstrated, in the case of unvulcanized sheets, by Hock[75] and by Feuchter.[76] Test strips elongated to 6½ times their original length had a density of 0.942 in the elongated state (0° C.) and a density of 0.923 when relaxed, thus showing an increase of 2 per cent in density on elongation. Both Feuchter and Kirchhof later investigated the density as a function of the elongation more thoroughly. In this connection mention should be made of the interesting discovery of Feuchter that rubber which has been slowly "frozen" by being stored in a cold warehouse has a density greater by 1.6 per cent than the same rubber when thawed out again. (*See also* p. 432.)

Older Work and Theories Concerning the Elongation of Rubber. If the behavior of rubber was to be in qualitative agreement with the second law of thermodynamics (as predicted by Thomson) it was at first anticipated that it would show a negative temperature coefficient of linear expansion. Lebedew,[77] however, showed that the density of stretched rubber decreased with increasing temperature. The decreasing density means that the volume coefficient of expansion must be positive. The fact that the length decreases and the volume increases with increase in temperature leads to the conclusion that the coefficient of linear expansion in the direction of the elongation is negative, while the coefficient of expansion in a direction perpendicular to the elongation must be positive. This anisotropy of stretched rubber has been investigated by Bjerkén, who studied the double refraction of thin rubber sheets after Kundt, Scherr-Thoss, and Pulfrich[78] had observed that rubber becomes dichroic when stretched or pressed. In the unstressed state, on the other hand, rubber is altogether an isotropic medium, with optical and mechanical properties the same in all directions. According to Bjerkén's observation, the index of refraction for the ordinary ray is larger than the index for the extraordinary ray, which characterizes rubber as an optically negative body.[79]

On the basis of these older discoveries, an explanation of the peculiar behavior was sought, and many hypotheses have materialized. Some of these hypotheses have been found to be useless, and others have been abandoned because of disagreement with experimental facts. In the present work, all of these theories are not discussed. (They have been reviewed in the studies of Slingervoet Ramondt, mentioned on p. 395.) The present discussion is confined to a few of the most fruitful theories. It must be kept in mind that even today, despite the accumulation of further experimental knowledge which will be considered shortly, there is no comprehensive hypothesis which explains all the phenomena. Accordingly, the reliability of our theoretical insight being what it is, we are not justified in ignoring any attempted solution which is fundamental and which is based on facts. The theory of R. Schmulewitsch[80] seems to be the one least open to objections, when all the

[74] *J. Ind. Eng. Chem.*, **13**, 1029 (1921).

[75] Qualitatively: *Kolloid-Z.*, **35**, 30 (1924). Quantitatively, [illegible] determined on a test piece wholly free from objection. *Z. Electrochem.*, **31**, 404 (1925).

[76] *Gummi-Ztg.*, **39**, 1167 (1925); also *Kautschuk*, **2**, 260 (1926); see also F. Kirchhof, *Kautschuk*, **2**, 151 (1926).

[77] *J. Russ. Phys. Chem. Soc.*, **13**, 246 (1881).

[78] Pulfrich, *Ann. Physik*, **14**, 177 (1882); see also Dissertation, Bonn, **1881**. Scherr-Thoss, *Ann. Physik*, **6**, 270 (1879). Bjerkén, *Ann. Physik*, **43**, 818 (1891). In reference to double refraction, see particularly p. 418 and p. 466.

[79] See also the work of L. Schiller in regard to the dielectric constant of elongated rubber; p. 418. Another investigation by M. Kröger (p. 466) shows positive double refraction.

[80] *Ann. Physik*, **144**, 280 (1872).

facts are considered. This theory ascribes to the rubber the positive linear thermal expansion characteristics of solids, and explains the contraction as the result of an extensive change in the elastic reaction due to the rise in temperature. The anomalous behavior of rubber with respect to its extensibility is thus explained, and it is obvious that the elongation of rubber involves a structural phenomenon, the effect of which is superimposed upon the normal behavior of the rubber. The nature of this structural phenomenon is as yet undetermined, but with further experiments it may be determined more and more definitely.

In order to find an adequate explanation of the behavior of rubber, there must be developed some concept of its physical structure from which information regarding the elastic behavior of the rubber can be derived. Mallock [81] compared rubber to a mixture of oil and chalk, from which a plastic stick can be formed. Such a stick exhibits considerable extensibility as long as the oil forms the continuous medium in which the chalk is dispersed. The fundamental part of this conception is the assumption of two phases, one of which is rigid while the other is mobile. The combination of these two elements results in a structure having elastic properties. A further development of this polyphase theory was offered by Fessenden.[82] He conceives of rubber as consisting of a combination of a soft-plastic with a hard-elastic medium, as in a model composed of spherical copper shells filled with water. An elliptical deformation of such a structure permits a considerable linear elongation without excessively straining the solid shell. Assuming that the rubber is composed of adjacent solid portions (corresponding to the copper in the analogy) and of a plastic mobile substance (corresponding to the water), the great extensibility of rubber can be pictured. Cheneveau and Heim [83] make the opposite assumption that a solid nuclear substance is surrounded by a soft shell. The original ready extensibility depends upon the deformation of the soft shell at first. Just short of the breaking point the solid nuclei are pulled apart, considerable force being required. In a similar manner R. W. Lunn [84] attempts to explain the elastic behavior of rubber and the Joule effect by considering the rubber to be a very viscous liquid in which are suspended spherical particles filled with liquid. These theories leave the question open as to the exact nature of the two constituents and as to which constituent forms the disperse and which the continuous phase.

Wolfgang Ostwald's Theory of Isocolloids. An answer to this question had already been furnished by Wolfgang Ostwald,[85] long before Hauser's investigations by means of the micromanipulator (*see* p. 56) had cast light on the two-phase nature of the latex particles. Ostwald's explanation involved the conception of "isocolloids" or "isodispersoids," which terms had originally been proposed by Ostwald himself. Plastic sulfur, styrene, metastyrene, etc., furnish examples of such systems. "In these systems, the dispersing medium and the disperse phase are the same chemically, but differ from each other in that they are modifications of the same substance, such as monomers and polymers, allotropes and isomers, etc. In synthetic rubber the two phases are isoprene, butadiene, etc., in the monomeric and polymeric states. According to the physical stage of the polymerization process, a vary-

[81] *Proc. Roy. Soc. (London)*, **46**, 233 (1889).
[82] *J. Franklin Inst.*, **142**, 187 (1896); see also G. S. Whitby: "Plantation Rubber and the testing of Rubber," p. 257, Longmans, Green & Co., London, **1920**.
[83] *Compt. rend.*, **152**, 320 (1911); also see the further development with regard to the stress-strain curve, p. 403.
[84] *J. Soc. Chem. Ind.*, **44**, 247T (1925).
[85] Ostwald, Wo., "Die neuere Entwicklung der Kolloidchemie," p. 23. Th. Steinkopff, Dresden and Leipzig, **1912**.

ing structure may exist, which without doubt consists in the beginning of an emulsion of polymerized hydrocarbons in the monomer. As the polymerized disperse phase increases, the droplets unite to form a network, and then combine to produce a honeycomb structure enclosing drops of the monomer, which thus becomes the dispersed phase. This process is similar to the setting of gelatin, agar, etc., according to the theories of W. B. Hardy. In natural rubber there is in addition the secondary coagulated 'heptogen' membrane of protein, which is formed by adsorption and which surrounds the latex particles. Natural rubber is thus a complex isodipersoid."

The Joule-Effect in Muscles and other Animal Tissues. It should be mentioned here that phenomena corresponding to the Gough-Joule effect have been observed in gutta-percha and above all in biological substances. On account of the obvious relationship of these phenomena to those occurring in the case of rubber, it appears desirable to give brief mention of the pertinent literature, with the object of facilitating a mutual interest in various fields of work. On account of observations of the Joule-effect in muscle fibers, physiologists have long been particularly interested in the phenomenon. The treatment of this subject by Schmulewitsch [86] *(see* p. 416) gives evidence of this interest. The writer is greatly indebted to Prof. W. J. Schmidt (Giessen),[87] who has taken great interest in the submicroscopic structure of animal tissues, for information regarding the experiments and the literature of this field. By way of example, the elastic fibers from the fins of sharks may be mentioned. These fibers shorten themselves by about one-third of their original length in hot water, which would be an unusual shortening in the case of rubber. Moreover, collagen, the substance of sinews, shows a thermal contraction which has been found to be similar to that exhibited by rubber. Finally, the elastic tissue of the cervical ligament of cattle shows a similar shortening effect, which is reversible up to a temperature of 60° C. In all these investigations the polarization microscope has proved to be a valuable instrument.

The Effect of Elongation on the Dielectric Constant. Before we pass on to a discussion of the influence of later experimental results upon the development of our theoretical ideas, we should consider the conclusive work of L. Schiller [88] concerning the change in the dielectric constant of rubber produced by tension in the direction of the lines of force. This work appeared in 1911, but unfortunately seems to have been practically unnoticed by workers in the field of rubber. Otherwise it would have greatly accelerated the systematic investigation of the anisotropy of elongated rubber. It is to be regretted that in discussing this matter later works have received first attention; unfortunately the author must also answer for his delayed recognition of this work. Fundamentally, the same physical measurement is made when the dielectric constant is determined by means of low-frequency, invisible electric waves as is made when the double refraction is measured by means of the high-frequency waves of visible light. However, if the key to

[86] Schmulewitsch, *Med. Jahrb.*, **1** (1868); of the newer literature in regard to the Joule-Effect in muscles, the following should be noted: A. V. Hill, *Naturwissenschaften*, **12**, 520 (1924); and the contribution of O. Meyerhof in regard to the thermodynamics of muscles in the "Handbuch der normalen und pathologischen Physiologie," by A. Bethe, G. von Bergmann, G. Embden and A. Ellinger, Vol. 8, pp. 1 and 505. See also the contribution of the same author in "Handbuch der Physik" (by Geiger and Scheel), Vol. 11, p. 260.

[87] *Arch. exp. Zellforschung*, **6**, 350 (1928); in addition *Z. Biol.*, **81**, 193-218 (1924) (Elastic fibers); E. Wöhlisch, *Z. Biol.*, **85**, 379-96 (1926) (Cervical ligaments); and E. Wöhlisch and Mesnil de Rochemont, *Z. Biol.*, **85**, 406-434 (1926) (Thermodynamics of the heat transformation of collagens).

[88] Dissertation, Leipzig, **1911.** See also p. 466 and p. 469 of this book.

the nature of the deformation is to be found in such measurements, the low-frequency waves would have an advantage, in that the resonance frequency of the molecules would not then have a disturbing effect on the results. Thus L. Schiller found a positive double refraction in contradiction to the previously cited result of Bjerkén. The application of this result to the problem of explaining how the anisotropy of elongated rubber comes about requires the use of the theory of O. Wiener [89] in regard to the dielectric constant of non-homogeneous bodies. On the basis of the observed positive double refraction and of the decrease of the dielectric constant with elongation—a decrease from 3.67 to 3.51 for an elongation of 30 per cent in the case of a vulcanized Para sheet (sp. gr. 0.95)—Wiener's theory leads to the following conclusion: the deformation results merely in an isotropic arrangement of the molecules, while the molecules themselves experience no other change. The anisotropy changes in a manner that would correspond to a rod-shaped arrangement of the molecules. Assuming that the dielectric constant itself is unchanged, it follows that either the molecules are elongated in the direction of the pull or that the molecules, which may normally be oblong, are orientated from a random arrangement to one in which their long axes are parallel to the direction of pull.

Unfortunately, this work did not at first lead those interested in rubber to attempt the explanation of the Joule-effect on the basis of the anisotropic structure of elongated rubber. It was only after the use of synthetic products and the introduction of organic accelerators had furnished a powerful impetus, that the manufacture of rubber goods emerged from the empirical state, and the chemists began to be interested in the fundamental properties of their unique raw material. In the last few years the problem of the structure of rubber has been attacked anew in many places. Further conclusions have been reached concerning the structure of rubber, both in its usual form in raw rubber and in its original form in latex. These conclusions are now to be discussed.

Theoretical Explanation of the Gough-Joule Effect and the Fiber Structure of Rubber.* Taking up the study of Joule's experiment Hock [90] turned first to the peculiar properties of raw rubber which can be observed in strips of Para rubber or smoked sheets. Joule had given up the study of raw rubber because the prominence of the elastic after-effect was detrimental to the reproducibility and to the interpretation of his results. Hock believed he would find a key to the theoretical explanation of the Joule-effect in the marked dependence of the elastic properties of raw rubber upon the temperature. Since the elastic properties of raw rubber are much more dependent upon the temperature than are those of vulcanized rubber, it was expected that far-reaching conclusions would result from this study. It is well known that the elastic behavior of vulcanized compounds is not greatly affected by temperature changes within a rather wide range (between $-20°$ C. and $+120°$ C.), whereas unvulcanized rubber changes from a state of elastic hardness to one of unresisting softness within the same temperature range. Even at room temperature, the elasticity of raw rubber has disappeared to a re-

[89] *Physik.-Z.*, **5**, 332 (1904); *Leipziger Ber.*, **61**, 113 (1909); **62**, 256 (1910). In reference to the theory of non-homogeneous bodies, see also Ambronn and Frey, "Polarisationsmikroskop," Akad. Verl.-Ges., Leipzig, **1926.**

* Translator's Note. A similar explanation of the Joule effect has been brought forward independently by C. R. Boggs and J. T. Blake [*Ind. Eng. Chem.*, **22**, 748-55 (1930)] in connection with their determinations of the electrical and other physical properties of raw and vulcanized rubber. — N. J.

[90] *Kolloid-Z.*, **35**, 40 (1924).

markable extent. Artificial rubber made from polymerized dimethylbutadiene shows a still greater dependence of this kind upon the temperature, and this dependence remains to a marked degree even in the vulcanized state. Moreover, the age and previous history of the test piece always exert a marked influence on its elastic behavior.[91]

If a ring cut from a slab of unvulcanized rubber be elongated even to a considerable degree at room temperature, it will retract almost to its original length when the tension is released. If the ring be elongated and held at an elongation just short of the point of rupture, an extremely large elastic after-effect will be noted since the ring will now have a permanent set of from 70 to 80 per cent of the preceding elongation. Feuchter has studied this experiment systematically, and has called the quick intensive type of elongation "racking." The results of this very interesting investigation, which have become known in terms of an extensive new terminology, will be given consideration later (p. 433). In the meantime an attempt at a fundamental explanation of the best-known of all the phenomena, the Gough-Joule effect, will be made.

A ring of rubber elongated as described above will remain in that state for any length of time at room temperature, but will immediately begin to twist, curl and draw together if touched by the warm hand or if immersed in warm water. In 1924, Hock[92] gave a theoretical explanation of this behavior, which was in complete agreement with the conclusions of L. Schiller with reference to the assumed structure of rubber, although at the time he was unfortunately not aware of Schiller's investigation. Hock postulated that with increasing elongation the elementary particles were almost completely orientated with their long axes in the direction of pull, a fact which is suggested by the observations of Bjerkén on double refraction. It was assumed that the molecules or quasi-molecules were rod-shaped and that the close packing of these elements which resulted from the elongation made it possible for the molecular or van der Waal forces to come into play and hold these elements together. In analogy to the Joule-Thomson effect in real gases, it was to be expected that a certain quantity of heat would be set free, due to the energy change involved in the action of the van der Waal forces when the rubber was elongated, and that this heat could be considered as a latent heat of transformation.[93] The aligned elements are obviously so immobile and so tightly bound together in their new positions that the restoring force is not sufficient to move them. Thus the work of elongation which is stored up in the form of potential energy of the elastic system is not manifested by any outer tension, and it is necessary to increase the mobility of these elements by increasing their thermal energy and thereby weakening their cohesive forces before they will return again to their original positions. This explanation makes it clear why it is that the rigid, elongated rubber can be made to contract by heating, and why it is that the elongation in the first place can be easily "fixed" by cooling the elongated rubber in cold water. The explanation also makes it clear why the retracting force is greater, the higher is the temperature of the water in which the rubber is immersed in order to bring about retraction (Fig. 72). A crude rubber ring of the di-

[91] J. Ostromislensky introduced into the classification of elastic materials the concept of "dead temperature" and "elastic temperature." When with decreasing temperature a substance is transformed into a rubber-like solid, it is said to have passed from the "dead" to the "elastic temperature." *J. Russ. Phys. Chem. Soc.*, **47**, 1374-1455; see also *J. Chem. Soc.*, **110**, I, 54 (1916).

[92] *Kolloid-Z.*, **35**, 40 (1924).

[93] In regard to the basis for the concepts of "heat of fusion" and "heat of transformation," *see* p. 456.

mensions of the usual test ring can raise a considerable weight (1 kg.) through considerable distance when it is made to retract by heating. Of the total capacity for performing work which is stored up in the rubber by the elongation, the amount which can be recovered in the performance of outside work by retraction depends upon the inner friction, which decreases as the temperature is raised. This consideration has already been suggested in connection with the temperature function of elastic hysteresis. (*See* p. 408.)

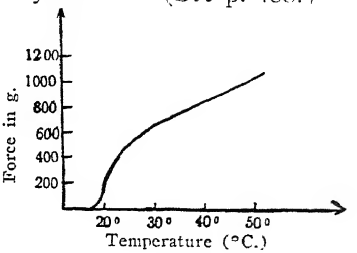

Figure 72—Relationship between the force of contraction and the temperature of relaxation of stretched, rigidified raw rubber. (According to L. Hock.)

The influence of the temperature upon the phenomenon in question can be determined in an exact manner by immersing the elongated ring in water. Under these conditions, it is found that the ring retracts at temperatures above 22° to 23° C., whereas it remains rigid at temperatures below 20°.[94] There is thus a temperature lying between rather narrow limits at which the force of the stored-up potential energy is just able to overcome the inner cohesive forces and the resistance to moving. It is therefore possible to observe a characteristic transformation point for the relaxation of the latent elastic energy of raw rubber in the elongated state in which it is spontaneously hardened. The transformation takes place with the absorption of a quantity of energy which enters into the phenomenon as latent heat. Hock has called this point the "melting point." These facts are in agreement with the theoretical concept of the fiber-structure of elongated rubber. This fiber structure is maintained by the activity of the molecular forces between the structural elements, which are of an anisotropic form and which are arranged in an anisotropic manner when the rubber is elongated. As soon as the thermal motion of the molecules exceeds a certain limit, the mutual attraction between them is insufficient to maintain this elongated arrangement. It is to be expected that x-ray photographs should give additional information as to the structure of elongated rubber. In a section devoted exclusively to these important x-ray investigations, the work of J. R. Katz, who was the first to apply the method successfully, will be discussed. (*See* p. 443.)

L. Hock[95] has furnished a striking proof of the fiber structure of rubber by cooling the elongated and stiffened raw rubber to the temperature of liquid air and breaking it into pieces by striking with a hammer. (*See* Fig. 73.) The resulting fibers, which are spread apart into a fan shape by the blow, form parallel bundles extending in the direction of the elongation. The fibers are probably made up of stretched-out chains of molecules, in accordance with the concept developed by H. Staudinger.[96] If the blow be made by

[94] See the special study of LeBlanc and Kröger in regard to the dependence of the relaxation temperature upon the elongation temperature, page 429.

[95] Z. *Elektrochem.* (Bunsenvortrag), **31**, 404 (1925); also *Gummi-Ztg.*, **39**, 1740 (1925); *Kautschuk*, **1** (Oct., 1925).

[96] The thorough explanation of Staudinger's proof of the high-molecular structure of rubber and the assumption of extended molecular chains is presented from a chemical and physical-chemical point of view in the following treatments: *Ber.*, **57**, 1203 (1924); G. Mie, H. Staudinger (with J. Hengstenberg, H. Johner, R. Signer) *Z. phys. Chem.*, **126**, 425 (1927). See also: *Kautschuk*, **1** (Aug., Sept., 1925). For the historical note by H. Staudinger, see *Gummi-Ztg.*, **43**, 759 (1929); (see p. 454, footnote 167).

a blunt chisel in a direction perpendicular to the direction of elongation, the cracks still take place in the lengthwise direction, running along the surfaces of least cohesion. In contrast to the elongated rubber, unstrained rubber at the temperature of liquid air breaks up like glass into irregularly formed chips.

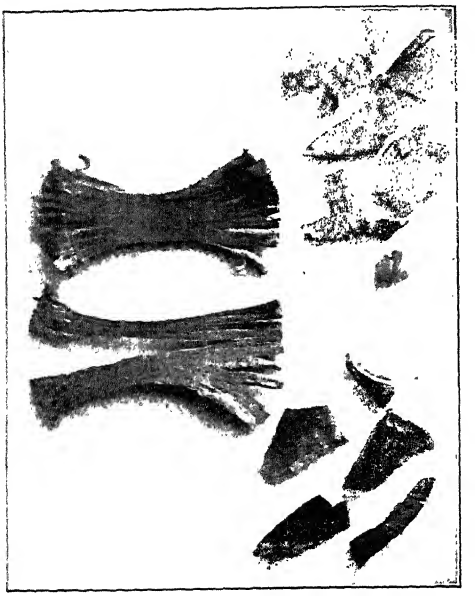

Figure 73—Structure of raw rubber as obtained at the temperature of liquid air. Left: Stretched raw rubber split into fibers. Right: Unstretched raw rubber split into fragments.
(According to L. Hock.)

Furthermore, it is easy to pull apart the frozen and split-up rubber along the seams with tweezers while an artificial cut started perpendicular to the direction of elongation cannot be extended without further cutting. If the shredded slab be allowed to relax as a consequence of heating, it is no longer easy to tear the bundles apart along the direction of the cracks. In regard to tearing, the rubber then shows the same behavior in both crosswise and lengthwise directions, because there is no longer any preferred direction in the arrangement of the molecules. The tearing experiments can be made as described by merely freezing the rubber in a freezing mixture. According to H. Feuchter,[97] if a strip of raw rubber, which has been made anisotropic, be cut along the fiber bundles for almost its entire length, all the little strips so formed will twist up into coils when relaxed.

The many forms of the associated phenomena, which are related to the Gough-Joule effect, are yet to be given individual consideration, after which the contributions in connection with the problem, which have been made by various investigators, will be evaluated. However, in order to give first a survey of the unmistakable inner relation between the structural and the thermodynamic phenomena, the heat transfer which is involved will be considered briefly. This may properly be considered here, since it answers some criticisms which have been made with respect to the theoretical explanation given above.

[97] *Kolloidchem. Beihefte*, **21**, 193 (1925). For photographic reproductions of these experiments, see also *Kautschuk*, **4**, 105 (1928).

The Origin of the Heat of Elongation. It was to be expected, especially inasmuch as chemically pure rubber had not been used in the experiments considered, that the rubber would contain certain resinous substances which give rise to considerable inner friction. At temperatures below a certain transition point, comparable to a "melting point," the resinous substances might bring about the rigidity of the elongated rubber. The heat of elongation would thus be explained as a frictional heat and could therefore not exceed the work used in elongating the rubber.[98]

On the basis of their discoveries with regard to the structure of the latex particles, Freundlich and Hauser [99] were led to assume that the heat of elongation was nothing but the heat of compression of the fluid enclosed in the particles. Here again, the amount of heat involved in the compression of the fluid particles could not be greater than the energy applied to produce the elongation. A first, approximate determination of the heat of elongation has been made by L. Hock and S. Bostroem. This measurement was made by allowing the thermal relaxation of a piece of rigid, elongated rubber (unvulcanized sheet) to take place in a water calorimeter. The results indicated the order of magnitude of the heat of relaxation to be about 10 cal. per gram for rubber elongated to seven times its original length. (A more exact determination of this heat will be described later.)[100] By comparing the result of the above-mentioned determination with the work required to elongate the rubber to the specified extent, it can be seen that the latter is only a small fraction (a few per cent) of the total heat transformation which is observed. Obviously, the work of elongation can not be the origin of that quantity of heat. The heat of elongation can be conceived only as the energy equivalent of a change in the physical structure of the rubber, as was first explained by L. Hock. Furthermore, the seat of this Joule heat cannot be in changes of state, involving dimensions of a microscopic order of magnitude. Rather must it be sought for in the molecular dimensions of the colloidal elements of the anisotropic rubber.

The Polyphase Nature of Rubber (Rubber as an Iso-colloid). It is obvious that, if the occurrence of the Joule effect is not connected with any microscopically observable mechanism between two phases—a more solid and a more plastic phase, such as E. A. Hauser [101] has found in latex—no conclusion in regard to the existence of polyphase rubber is apparent from the Gough-Joule effect. That is hardly necessary, since the polyphase nature of rubber is well established from other angles. The diffusion experiments of Caspari [102] and of H. Feuchter,[103] the separation of crude rubber into fractions which were physically different but chemically the same as accomplished by Pummerer,[104] the previously developed theory of Wolfgang Ostwald in

[98] In discussing an article by Hock (*Z. Elektrochem,* **31,** 408 (1925), Masing made the suggestion that a highly viscous substance in the rubber might be the cause of the Joule effect. Kröger also contributed to this idea, although his conception differed in that the highly viscous portion was supposed to be a higher polymer of rubber, while the rest of the rubber consisted of smaller molecules. However, all of these explanations must be rejected since the heat of elongation (as shown later) is significantly greater than the work of elongation, even if the latter were completely transformed into frictional heat. Since a considerable portion of the work of elongation can be regained, and thus must be stored in the rubber as potential energy, that part which may be transformed into frictional heat is negligible in comparison to the observed heat of elongation. These facts and considerations have evidently been overlooked by Ariano, who recently has attempted once more to explain the Joule heat of elongation as frictional heat. (*See* footnote, p. 401.)

[99] *Kolloid-Z.* (Zsigmondy Festschrift), **36,** 33 (1925).

[100] *See* p. 437; *see* also Bostroem, footnote 39, p. 405.

[101] See p. 56.

[102] *J. Soc. Chem. Ind.*, **32,** 1041 (1913); see also Stevens, *ibid.* **38,** 192T (1919).

[103] *Kollojdchem. Beihefte,* **20,** 434 (1925); in addition see p. 175, and also P. Bary's theory of solid solution p. 473 and p. 479.

[104] *Ber.*, **55,** 3458 (1922); **60,** 2148 (1927); and especially p. 166 in this book.

regard to the iso-colloidal nature of rubber, and Staudinger's theory of the temperature-conditional equilibrium between macromolecules of widely different sizes, are all in the best of agreement with the microscopically determined polyphase structure of rubber. In fact, the characteristic elastic, thermal and other physical properties of a given rubber preparation must be decidedly influenced by its relative content of large molecules more or less colloidal in size.

H. Hopff and G. von Susich* [*Rev. gén. caoutchouc*, **7**, 23 (1930); *Kautschuk*, **6**, 234 (1930); *Rubber Chem. Tech.*, **4**, 75 (1931)] have shown by x-ray analysis that "the hydrocarbons of gutta-percha and balata are identical, but differ from those of rubber. The hydrocarbon of gutta-percha exists in two polymorphous modifications, whose transformation point is about 60° C., but depends upon the impurities present. The modification stable at room temperature (gutta-α) is crystalline even in the unstretched state. The modification stable above 60° C. (gutta-β) is, on the contrary, amorphous in the unstretched state, like rubber at room temperature. By stretching when hot, it becomes crystalline and oriented, giving a fibrous spectrum by analysis. For the modification α, one can calculate from the fiber diagram of the stretched and cooled samples an identity period of 4.7 or 9.4 Å, respectively. The x-ray observations of Clark, Hauser and Ott, which are contradictory in certain respects, have been discussed and partly explained by the existence of the two modifications."

The Idea of Aggregation and Disaggregation. LeBlanc and M. Kröger [105] have pointed out the significance of the degree of aggregation and disaggregation with respect to the physical behavior of rubber. In using these terms, they have reference to the colloidal complex and not to the size of the microscopic latex particles. M. Kröger,[106] in discussing the colloidal phenomena connected with vulcanization, has stated that the size of the original latex particle has little influence on the quality of the rubber, surprising though it may seem. Obviously, the proportions of the lower aggregates and of the higher polymers are of much more importance than is the exact nature of the final agglomerated particle, which must be but loosely held together (*see* p. 431).

The Calender-Effect (Calender Grain). The size of the latex particle is no indication of the degree of polymerization. M. Kröger has supposed that when the rubber passes between the rolls, not only the original latex particles, but also the fragments, are crushed and flattened out, a supposition which is favored by the phenomena observed in connection with the calender effect. L. Hock [107] introduced the effect of the temperature upon the contraction force of anisotropic rubber (*see* p. 402) into the explanation of the calender effect. According to his idea, "dead-milled" rubber has been prevented from returning to its isotropic state because of the cooling it experienced as it passed over the cold roll. Along with the investigations of van Rossem,[108] Lunn,[109] and others, the thorough study of the calender-effect in unvulcanized rubber by W. de Visser [110] should be especially mentioned. His results show that the elastic behavior of a slab taken lengthwise is different from that taken crosswise, because of the anisotropy produced by the rolls. These results also show that the speed with which the rubber returns to the isotropic state, the completeness of the return, and the amount of the calender-effect itself, all depend upon the temperature of the rolls. The greater the

* Translator's note by N. J.

[105] See particularly *Kolloid-Z.*, **37**, 205 (1925).

[106] *Kolloid-Z.*, **33**, 267 (1924). For other communications from the same author in regard to the relation of the aggregation and close packing of rubber to the elastic properties of rubber, see *Gummi-Ztg.*, **40**, 2319, 2373 (1926); **40**, 782, 1893 (1926).

[107] *Kolloid-Z.*, **35**, 47 (1924).

[108] *India Rubber J.*, **62**, 343 (1921). Wiegand believed that the calender-effect is certainly not related to the Joule-effect. [*India Rubber J.*, **62**, 733 (1921)].

[109] *India Rubber J.*, **65**, 565 (1923).

[110] Dissertation, Delft, J. H. de Bussy, Amsterdam, **1925**; See also *Gummi-Ztg.*, **40**, 457, 511 (1925).

difference in speed of the rolls between which the rubber slab passes, the more marked is the anisotropy thereby produced. The results given in Table 5 show the amount of the calender-effect under various conditions of temperature. These data were obtained by de Visser on slabs about 1 mm. thick. These slabs had passed over a cold calender roll of varied temperature, after having been put through the two upper rolls, which were maintained at a temperature of 80° C. (*See* p. 459, footnote 186.)

TABLE 5.—*Influence of the Temperature of the Cooling Roll on the Calender-Effect (according to de Visser).*

		Results of tensile tests			
		Parallel to direction of calendering		Perpendicular to direction of calendering	
Temp. of Cooling Roll ° C.	Thickness of Slab mm.	Tensile Strength kg./sq. cm.	Elongation per cent	Tensile Strength kg./sq. cm.	Elongation per cent
9	0.85	15.00	118	2.93	513
25	1.00	11.70	140	2.37	497
35	1.00	8.49	164	1.65	514
45	0.95	6.28	237	1.53	558
55	1.10	3.28	271	1.42	364
65	1.10	2.33	453	1.38	472
80	1.10	1.71	485	1.43	500

The anisotropy of calendered slabs has also been proved by the double refraction and dichroism which they exhibit, by the existence of x-ray interference patterns, and by the increased density.[111]

Preliminary Survey of the Fundamental Phenomena. In order to obtain a survey of the subject which will not be overburdened with details, the various mechanical, thermal, and structural phenomena which are connected with the Gough-Joule effect (together with the influence which these phenomena have on the technical properties of rubber) have been considered only in a general way. The particulars in connection with the various phenomena and also the additional results from the investigations of the structure of rubber, which have been made possible by the use of x-rays, are now to be gone into more thoroughly. Consideration is also to be given to the theoretical concepts of the various investigators.

In summarizing, it may be said that the conclusions drawn from the optical double refraction, the change in the dielectric constant, the increase in the density, and from the related mechanical and thermal behavior of rubber, lead to a picture of the inner structure of rubber which explains the observed facts to a considerable degree. The theory developed is of a synthetic nature in the sense that it provided for the first time (1924) a theoretical explanation of the previously determined relationships between the observed properties. Including the yet-to-be considered results of x-ray investigations, which have shown the existence of crystal interference (Katz, 1925), there is available unmistakable evidence of a phenomenon of orientation which accompanies the elongation of the rubber (in agreement with the idea presented above). Through the more extensive x-ray investigations (Hauser and Mark, 1926; Mark and von Susich, 1928) the insight into the structure of rubber has been materially extended and clarified. It is believed that the next most important result of these measurements was to show that the number of aligned particles or micelles increases in proportion as the elongation increases. This was first determined quantitatively by Hauser and Mark. (*See* p. 446.)

[111] In regard to the persistence of calender grain after vulcanization, see W. B. Wiegand and H. A. Braendle, *Ind. Eng. Chem.*, **15**, 259 (1923).

Detailed Section

In the detailed discussion which follows, the dependence of the mechanical properties upon the temperature will be treated first. The discussion will then be extended to include the determination of the latent heat of transformation, which is involved when the rubber changes over from the isotropic into the anisotropic state. Finally, the x-ray investigations of the structure of rubber will be discussed.

Mechanical Experiments Connected with the Gough-Joule Effect, and their Theoretical Explanation

The Gough-Joule Effect in Synthetic Rubber and in Vulcanized Rubber. The phenomenon of a transition point similar in nature to the melting point of crystalline substances, which is observed in crude rubber, is also found to exist in synthetic rubber. To be sure, a lower temperature is required for the fixation of the elongation, as has been shown by the work of L. Hock and P. Siedler [112] on W and H methyl rubber. Above a temperature of about 10° C. the elongated strips contract again after the tension is released. If synthetic rubber, which has been made anisotropic, is cooled to the temperature of liquid air, and pounded with a hammer while in the hard frozen state, it develops the same fibrous separations running in the direction of elongation as are found in raw rubber under similar treatment, although the phenomenon is not so marked. Pieces which are frozen without being elongated break up into irregularly shaped fragments when pounded. This behavior shows that natural and synthetic rubbers are of similar physical structure, in addition to being chemically related (which does not at all mean they are chemically identical). There is, however, a marked difference between the two kinds of rubber, as is shown by technological observation, but this difference may perhaps not be eliminated entirely by changing their physical structures and states of aggregation. It may depend upon their chemical constitution, even if one is convinced that the physical structure—which depends upon the molecular structure—is of the greatest importance in determining the elastic behavior of rubber. In fact, the relationship between cohesion and valence is so close in rubber that it is idle to try to draw a sharp distinction between them. (*See* pp. 454 and 490.)

According to the orientation theory, the lesser degree of aggregation which must be ascribed to synthetic rubber means that there are fewer suitably large, molecular complexes to offer the contact surface which is required for the van der Waal forces to manifest themselves. Only at lower temperatures are these forces able to maintain the rubber in an elongated state, since at higher temperatures the molecular motions are so great as to overcome the effect of these forces. In any case, natural rubber is to be considered as a progressive system of polymers. In other respects, the parallelism of the Gough-Joule effect permits the same explanation for both the natural and the synthetic rubber.

As has been known since the time of Joule,[113] the effect now under consideration is easily observed in vulcanized rubber. Naturally, the strength of the effect depends to a great extent upon the particular type of compound and upon its previous treatment. High quality, compounded vulcanizates may show a very marked action, as was demonstrated, for example, by the operation of Wiegand's pendulum. (*See* p. 413.)

[112] *Kautschuk*, **2**, 88 (1926).

[113] *Trans. Roy. Soc. London*, **149**, 91 (1859).

If an elongated ring of vulcanized rubber is cooled merely by water or ice, there will be no appreciable fixation of the deformation. After the release of the tension there is only a relatively small elastic after-effect, which can, however, be eliminated with the performance of external work by placing the ring in hot water. There can be no particularly high degree of anisotropy in connection with this slight after-effect, but merely a residual amount of potential energy which can exhaust itself only after the inner friction has been decreased by warming the test piece. A different result is observed, however, if the elongated ring is cooled to an appreciably lower temperature, such as that of carbon dioxide snow. A state of the highest anisotropy is preserved in such a case. L. Hock and P. Siedler [114] have shown that an elongated strip of vulcanized rubber will also exhibit a fibrous structure when cooled in liquid air and then shattered. The Joule effect in vulcanized rubber is another proof that the heat which is liberated on elongation cannot be the heat of compression of an enclosed quantity of fluid. Even if the microscopic structure of crude rubber is destroyed by "dead milling" on a cold mill, the compound which is prepared from the raw rubber by vulcanization with heat will show the same Joule effect.

A vulcanizate of artificial rubber is like that from crude rubber in that it permits an easy fixation of its anisotropy. By assuming that the polymerization in methyl rubber, which flows more readily at high temperatures, is considerably less extensive than it is in raw rubber, and that the vulcanization process involves an increase in the degree of polymerization, the following explanation can be made: the lesser degree of polymerization in the artificial rubber means that a correspondingly smaller number of suitably large molecular complexes offer the contact surface which is required for the van der Waal forces to manifest themselves and thus lead to orientation. Only at lower temperatures, at which the aggregation of the rubber is greater, are these forces able to achieve the fixation of the extended state. The fact that the potential energy is less at low temperatures also tends to favor this fixation. Larger molecular aggregates are formed when this material is vulcanized so that its structure is then similar to the structure of natural raw rubber.[115] In fact, the aggregation increases considerably as vulcanization progresses, and the energy capacity of the rubber is thereby increased. The strong contracting force makes it impossible to "freeze" the elongation at the higher temperatures. Furthermore, it may be supposed that the inner cohesive forces pass through a maximum as the degree of vulcanization increases, since with a certain coarsening of the structure the number of points between the colloid particles where the van der Waal forces may come into action is greatly decreased.

"Vulcanization by Cold" (according to M. LeBlanc and M. Kröger). LeBlanc and Kröger [116] have investigated the change in the state of aggregation as influenced by temperature and by vulcanization. Their experiments have led to some extremely important conclusions in regard to the nature of the elastic state into which rubber is brought by vulcanization. From experiments on orientation at low temperatures, they were led to believe that under such a condition, the crude rubber acquired elastic properties which approximate those of the vulcanized product. To confirm this belief stress-strain curves were obtained for raw rubber rings at temperatures between the freezing point of water and –60° C. The permanent set was also

[114] *Kautschuk*, **1**, (Oct. 1925).
[115] See L. Hock, *Kautschuk*, **2**, 65 (1926).
[116] *Kolloid-Z.*, **37**, 205 (1925).

measured, in order to show to what extent the cold raw rubber was like the vulcanized product.

Test rings of the usual type were stamped out of calendered, cold-pressed slabs of crude rubber of different kinds (crepe, hard Para, soft Para and Congo rubber). An elongation device attached to a Schopper testing machine made it possible to elongate the rings while they were immersed in a cold bath (cooled alcohol) which controlled the temperature of the test pieces accurately.[117] To furnish a comparison with the properties of vulcanized rubber, a mixture of the crepe with 7 per cent of sulfur was vulcanized for various lengths of time at 138° C., and tested as usual, except that the tests were made at the various low temperatures used for the raw rubber. As is shown by the complete tables in the original work, the increase in the time of vulcanization had the same effect as a decrease in the temperature at the time of test. The tensile strength increased at first as the temperature was decreased, passed through a maximum, and then fell off markedly at temperatures below —50° C. The properties below —60° correspond to those of ebonite. The permanent set was also determined by measuring the length of the ring, which originally had an inner diameter of 16 cm. Table 6 gives a summary of the results.

TABLE 6.—*"Vulcanization by Cold" (according to LeBlanc and Kröger).*

Load in kilograms	Elongation in per cent at various temperatures				
	— 15° C.	— 25° C.	— 34° C.	— 50° C.	— 55° C.
1	20	25	0	0	0
2	100	60	0	0	0
3	270	160	50	30	30
4	370	260	200	70	40
5	425	320	275	120	50
6	470	360	320	200	90
7	500	400	370	250	200
8	530	440	400	300	290
9	—	470	430	330	340
10	—	490	460	360	390
12	—	515	490	430	430
14	—	540	510	490	470
16	—	565	540	540	530
18	—	590	560	580	560
20	—	610	580	610	570
25	—	—	610	650	—
30	—	—	640	680	—
40	—	—	670	710	—
Permanent set in cm.	—	19.5	19.0	17.5	17.0

It was also found that the highest loading corresponded closely with that found when the rubber was vulcanized to the optimum state. The authors reached the following conclusions after determining the tensile strengths of samples vulcanized for from one to five hours, the tensile tests being conducted at temperatures between + 80° and — 60° C.:

"Raw rubber shows good elastic properties at low temperatures within a rather narrow temperature range. If the rubber is under-vulcanized with sulfur in the usual manner, this temperature range is widened toward higher temperatures. This region of good elastic properties is shifted up as far as room temperature by further vulcanization." The permanent set was determined by measuring the length of the ring after it had been immersed in

[117] Tests of tensile strengths at the temperature of liquid air had previously been made by Polányi and Schob (1924). These tests will be considered again on p. 431. In regard to the methods of execution of this kind of elongation and tensile tests see p. 516.

water at about 20° C. immediately after the break. The permanent set was less the lower the temperature at which the ring was elongated, or the more the rubber was vulcanized. In this regard also there was complete agreement between the behavior of the normally vulcanized rubber and that which was vulcanized in a purely physical manner by the cold. From this discovery, it is obvious that the striking change in structure which occurs in vulcanization is of a physical nature. On the basis of the idea of aggregation and disaggregation, which was first applied to the changes in state of rubber by Harries,[118] and on the further basis of Staudinger's [119] concept of an equilibrium between smaller and larger molecular associations (which equilibrium is shifted by temperature changes), LeBlanc and Kröger came to the conclusion that the same increased aggregation which was brought about by the low temperatures in their experiments is effected by the action of sulfur in the usual vulcanization by heat. However, it must not be overlooked that "vulcanization by cold" results in a reversible change in state, whereas actual vulcanization is of value for the very reason that it is irreversible and leads to a product which possesses uniform elastic properties over a rather wide range of temperatures. Without doubt, the distinguishing contribution which the sulfur makes to this irreversibility must depend on its chemical combination. Possibly an extremely small quantity of sulfur may suffice for this action, but sulfur is indispensable if the vulcanization is to give the rubber a structure which is independent of the temperature, albeit the vulcanization itself consists essentially of a change in physical structure. Without going into the chemistry of the process, it can be imagined that the sulfur forms bridges here and there between the aggregates, which prevent any return to their former state of independence of one another or any possibility of disaggregation at the temperatures which prevail for the normal uses of rubber.[120] With this concept in mind, it seems possible that some other means may be devised for producing structural changes such as occur in vulcanization, and of making these changes irreversible.[121]

The Relation Between the Elongation Temperature and the Contraction Temperature. The experiments on the thermal relaxation of elongated crude rubber which were discussed on p. 421 have been carried further by LeBlanc and his collaborators, who have obtained important results while working at low temperatures. They found that the manner in which the elongated rubber retracted depended markedly upon the temperature at which the elongation had been made, as well as upon the temperature to which the ring was subjected after the elongation. They also found that when the loading was of short duration, the test piece returned almost entirely to its original length when the load was removed. If the load were allowed to act

[118] *Ber.*, **56**, 1048 (1923). Here Harries distinguishes between chemical polymerization and the idea of aggregation, and defines aggregation as the mutual adsorption between two or more dispersed phases.

[119] *Ibid.*, **57**, 1206 (1924); **59**, 3019 (1926).

[120] This disaggregation may be brought about by the so-called reclaiming of old rubber, which does not at all consist of a chemical separation of the sulfur and the restoration of the pure hydrocarbon, but rather of a breaking up of the aggregates by thermal or mechanical treatment. In spite of the combined sulfur which remains from the previous vulcanization, this reclaimed rubber requires the addition of still more sulfur if it is to be vulcanized again. That is, new sulfur is required to bind together the aggregates as they may now exist, by a bridge-building process similar to that occurring in the vulcanization of crude rubber.

[121] This last discussion, together with those on pp. 489 ff. of this book, represent, incidentally, the elaboration of a lecture on the subject of "Isomerization and the Problem of the Colloidal Structure of Rubber," presented by G. Fromandi to the Deutschen Kautschukgesellschaft in Hamburg, before the present manuscript was published. See *Kautschuk*, **4**, 188-190 (1928). The work of K. H. Meyer, *Z. angew. Chem.*, **41**, 935 (1928), which was published at about the same time, is in complete agreement with these ideas. This work was later supplemented by the communication of K. H. Meyer and H. Mark, *Ber.*, **61**, 1939 (1928).

for a longer time, retraction could be made to take place only at a higher temperature. The temperature at which practically complete retraction occurs (i. e., the "contraction temperature," according to LeBlanc and Kröger) depends to a striking degree upon the temperature of elongation. For example, a contraction temperature of about + 10° C. corresponds with an elongation temperature of — 30° C. Figure 74 shows graphically the relationship between

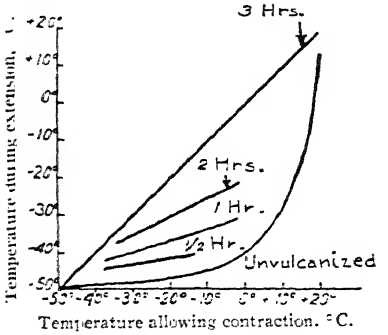

Figure 74—Dependence of the temperature at which contraction occurs, on the temperature at which extension was performed. (According to M. LeBlanc and M. Kröger.)

(Time of vulcanization shown on each curve separately.)

elongation temperature and contraction temperature for raw rubber and for cured samples of the rubber-sulfur compound previously mentioned. In the words of LeBlanc and Kröger,[122] "Increasing vulcanization narrows the range over which the rubber shows complete rigidity until the range vanishes altogether for a thoroughly vulcanized compound. Here also it may be seen that the vulcanization with sulfur does not introduce anything fundamentally new into the existing rubber system, but only makes it possible for an exceptional state which exists normally at — 50° C. to exist also at higher temperatures." For studying further peculiarities of the elongation phenomena which demand detailed description, reference must be made to the original work.*

LeBlanc and Kröger have given an explanation of the Joule effect which is quite analogous to the explanation which had previously been given by Hock and which we have already discussed. The explanation of LeBlanc and Kröger differs in the choice of the imagery but not in the fundamental ideas. The Joule effect is conceived as "the heat transfer involved in a peculiar type of wetting phenomenon [123] at the newly formed inner surfaces" of a specimen of rubber which has been made anisotropic by stress. "In it, therefore, must be included all those effects which are connected with the alignment of atom

[122] *Kolloid-Z.*, **37**, 209 (1925).

* Translator's Note. A practical application of the effect of cure on the relation between the temperature of elongation and the retraction temperature has been made by Gerke [W. A. Gibbons, R. H. Gerke and H. C. Tingey, *Ind. Eng. Chem., Anal. Ed.*, **5**, 279 (1933)], in the development of the so-called "T-50 Test for State of Cure." (This test is described in greater detail on p. 552)—N. J.

[123] Inasmuch as Kröger here accepts the idea which he had previously questioned (see p. 423); i.e., that the Joule effect is a matter of the action of molecular forces which are usually designated collectively as van der Waal forces, that positing favorable to the writer's older concepts [*Kolloid-Z.*, **35**, 48 (1924) and *Z. Elektrochem.*, **31**, 469 (1925)], must have been given up again. That is further indicated by the statement on p. 211 of LeBlanc and Kröger's article which questions the importance of the frictional forces as compared to the interfacial forces acting between molecular aggregates when the rubber is elongated and frozen. The explanations of the Joule effect offered by Hock and by LeBlanc and Kröger agree in general. If these hypotheses are compared an unnecessary confusion results (see for example Hauser and Mark [*Kolloid-chem. Beihefte*, **23**, (Ambronn-Festschrift) 72 (1926)]. These theories show a mutual agreement—in common with Wolfgang Ostwald's theory of the accidental formation of a space lattice, as well as with the "cell energy" theory of Klein and Stamberger (see pp. 456 and 481)—in opposing the explanation by means of the "swelling theory" (see p. 455).

groups on these surfaces, and which must bring about x-ray interference as a consequence of additional atom layers being influenced by the inner cohesion of large molecules."

The turbidity of elongated rubber is attributed by these same authors to air inclusions and the resulting optical inhomogeneity of the rubber-air system.[124]

The Structure Theory of LeBlanc and Kröger. This presentation of the experiments of LeBlanc and Kröger will be completed with a discussion of their conclusions in regard to the structure of rubber, which conclusions have been confirmed by experience. The molecular aggregates or "heaps," which arise from local variations in the degree of polymerization of the hydrocarbon, are taken to be of outstanding significance with respect to the elastic properties of rubber. The large aggregates form a sort of framework throughout a more or less slightly polymerized phase, and the interaction between the framework and the remaining substance is responsible for the elasticity of the rubber. The elastic property can be enhanced by vulcanization or by extreme cooling. The effect of the cooling can easily be explained, since cooling would result in a coarsening of the structure, due to the agglomeration of the particles. Thus there is a continuation of the aggregation process which remains stationary at higher temperatures, and a decrease in the dispersion takes place. The framework becomes stiffer; it increases in extent by additions from the less aggregated portion and thus further enhances its elastic properties. This hypothesis, which of course can be only indirectly confirmed by experiment, leads to the expectation that with still further aggregation, a decrease in the elastic properties would finally occur. It is worthy of note that the concept of a polymerization equilibrium with a large temperature coefficient, which had already been developed by Staudinger, fits readily into this picture of the structure (*see* p. 453).

The Increased Strength of Anisotropic Rubber (According to Pólányi and Schob). In order to determine whether or not the mechanical strength of rubber in the elongated state is greater than that of rubber in the normal state, Pólányi and Schob[125] have conducted tensile tests on soft vulcanized rubber at the temperature of liquid air. Such a comparison is obviously impossible at room temperature, since the normal rubber must first be subjected to the elongation process before the rupture occurs. However, the tensile test can be made at the temperature of liquid air without any appreciable deformation of the rubber taking place. Short flat strips of vulcanized rubber which were provided with heads for gripping were used in this test. The strips, which had a cross sectional area of 2 sq. mm., were broken by a load of 5 kg./sq. mm. at a temperature of 85° K. However, if the strips were elongated at room temperature to about five times their original length before being put into the same cold bath, no appreciable change in form was produced by a load of 20 kg./sq. mm. A force of 50 kg./sq. mm. was required to break these strips, and the break occurred at an elongation of about 800 per cent.

[124] LeBlanc and Kröger explain the decrease in volume which accompanies elongation, not as the result of compression, but partly as the result of the rearrangement of the molecules extending out from the interfacial surfaces, and partly as the result of the compression of the air-filled spaces. In regard to the density of elongated rubber, see discussion on p. 432 and also M. Kröger, *Gummi-Ztg.*, **40**, 2373 (1926). In addition, the idea of the action of compression is supported by M. Ruhemann and F. Simon, *Z. physik. Chem.* **A 138**, 1, (1928).

[125] *Mitt. Materialprüfungsamt Berlin-Dahlem.*, **42**, 22 (1924); see also the report in *Chem. Zentr.*, **97**, I, 2255 (1926); *Chem. Abstracts*, **19**, 1209 (1925).

The observed strengthening of the rubber, along with the maintenance of the elongation, has thus been brought about, by freezing after a previous warm racking. This strengthening effect is reversible, since it will disappear as soon as the rubber is allowed to return to its normal state by the application of heat. There is accordingly a marked difference between this reversible strengthening of rubber and the hardening of metals by cold working, which is an entirely different type of phenomenon.

Feuchter[126] has obtained significant results in connection with the phenomenon of the Gough-Joule effect along the line of the experiment of L. Hock, in which the anisotropic elongation of the rubber was fixed by cooling or by particularly intensive stretching. Feuchter has subjected the elongation and racking phenomena in connection with raw rubber to a further systematic study. Reference must be made to the original report of the author, because of the many details involved in a description of the experimental procedure. Likewise, it is possible to give only the essence of his theoretical concepts which are clothed in an exceptionally rich and unique terminology. We shall, therefore, limit ourselves to giving some of the experimental results.

Feuchter's Experiments on the Stretching of Raw Rubber. Feuchter investigated the dependence of the elongation phenomenon upon the velocity[126a] with which the deformation took place, and by the repeated racking of rubber he found a method by which the elongation could be made to reach the astonishing value of 10,000 per cent. That is, he succeeded in drawing out a thin raw rubber strip which was held between pincers from a length of one centimeter to a length of one meter. That was accomplished by cutting a short strip 5 mm. wide from a smooth slab of smoked Hevea sheet 2 mm. thick and racking it fifty times in succession, immersing it each time for a short while in water at a temperature of from 80° to 90° C. The elongation returned to 1,000 per cent when the strip was relaxed by heating in water at 70° C., and therefore the rubber was left in a new, normal, isotropic state. Feuchter[127] investigated the change in density up to an elongation of 4,000 per cent. The results of this investigation on the smooth sheet which he used are given in Table 7.

TABLE 7.—*Effect of Very Great Elongation (Racking) on the Density of Raw Rubber (according to H. Feuchter).*

Racking per cent	Observed density	Decrease in volume per cent
—	0.937	—
500	0.946	1.0
1000	0.950	1.4
2000	0.953	1.8
4000	0.953	1.8

It is important to note that the swelling (in benzene, for example) of the rubber which is racked so extremely, and which must therefore have a high degree of anisotropy,[128] is quite negligible. It is therefore possible to put the racked strip in a rubber solvent without any resulting shortening. A less extremely elongated strip will begin to swell immediately.

[126] *Kolloidchem. Beihefte*, **20**, 434, **21**, 171 (1925); also various communications in "Kautschuk" during the years 1926-28, and especially *Kautschuk*, **3**, 151 (1927).

[126a] *See* pp. 411 and 441 of this book.

[127] *See* p. 415 of this book.

[128] This is shown by the decidedly sharp x-ray interference patterns of rubber which has been subjected to this treatment; see Fig. 87, p. 448.

From a theoretical point of view, the dissolving and swelling phenomena presuppose some interaction between the dissolved substance and the solvent. According to the concept of valence in chemistry, this interaction amounts to a satisfying of the secondary valences; in the sense of physical chemistry, it amounts to a mutual action between electric fields of force. From this it may perhaps be assumed that as the rubber is elongated, the increasing interaction of the van der Waal forces (secondary valences) within the rubber itself puts such a strong demand on these forces that a reaction with the solvent is impossible or at least considerably more difficult.[129]

If the rubber be elongated quickly, the Joule heat does not have an opportunity to pass off during the elongation process. Hence, this quick elongation is an adiabatic process (W. B. Wiegand), whereas a slower elongation in which the heat is given opportunity to pass off is an isothermal elongation.

Feuchter has described an interesting cycle, to which we have already referred in part. This cycle is shown in Figure 75 and in Table 8.

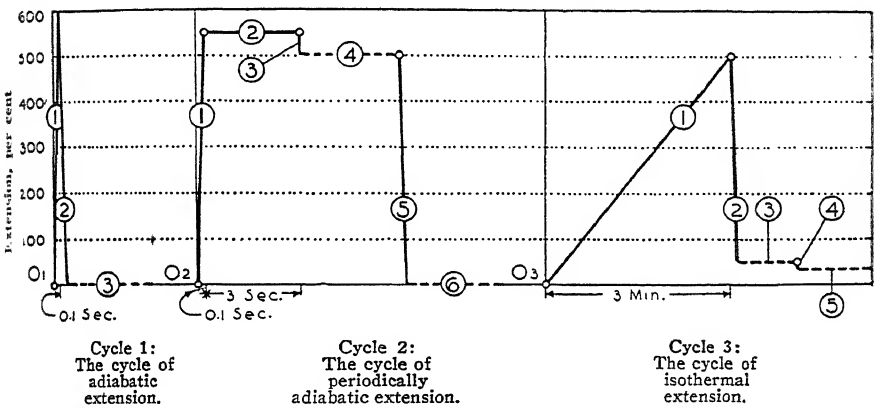

Figure 75—Graphical representation of adiabatic and of isothermal extension (according to H. Feuchter). The full lines represent elastic phenomena (changes of shape). The dashed lines represent elastic states or conditions which remain practically unaltered with time.

The figure and the table are self explanatory if it is kept in mind that "permanent elongation" is used to designate the elongation which persists after thermal retraction, while "plastic elongation" is used to designate the elongation which persists after thermal relaxation.

The theoretical concept which Feuchter developed in his investigation is similar to that of Fessenden[130] in certain of its fundamental aspects. In order to indicate the exact manner in which Feuchter has attempted to explain the relation between the structural and the thermal phenomena by the use of a quite unfamiliar terminology, his own words will be quoted:*[131]

[129] This idea was proposed by the author during the discussion at the second main meeting of the Deutschen Kautschukgesellschaft, Hamburg, Sept. 15, 1928. (Lecture of Dr. Loewen.) In regard to the relation between the secondary valence forces and the constitution of rubber, and in regard to the influence of these forces on the colloidal properties of rubber, see p. 491 and also G. Fromandi, *Kautschuk*, **4**, 189 (1928).

[130] See p. 417.

[131] See *Kolloidchem. Beihefte*, **21**, 171 (1925).

* Since Feuchter's terminology is so peculiarly his own, we have left this quotation in the German, rather than attempt a translation which would not convey the shades of meaning intended. V. N. M.

TABLE 8.—*Outline of Adiabatic and Isothermal Phenomena of Extension.*

Raw Material: Hevea sheets in smooth slabs; elastic and soft (not frozen).

Experimental Material: Evenly cut and marked strips, having a cross section of 2 mm. square.

Room temperature: 20° C.

V = process of extension. Z = state of elongation.

The percentages throughout are expressed on the basis of the originally marked length as 100.

The maximum extension.		The relaxation as dependent on time.		The thermal relaxation of the remaining racking: 2 min. in water at 60° C.
First Experiment: The cyclical process of adiabatic extension.				
Adiabatic extension to fracture. Time: 0.2 to 0.1 sec. Extension: 40 mm. to 280 mm. length, or 600%.	V_1	After the process V_1, the two parts of the marked test piece quickly retract, the retraction being from 280 mm. to 40.8 mm. Residual extension: 2%	V_2 Z_3	—
Second Experiment: Interrupted cycle of adiabatic extension.				
Adiabatic extension: Time: 0.2 to 0.1 sec. Extension: 20 mm. to 130 mm. or 550%	V_1	After process V_1, the strip was held at 550% elongation for 3 sec. . . . On release of the stress, a retraction occurred . . . from 130 mm. to 120 mm. length, with a resultant racking of 500%.	V_3	The strip in condition Z_3, after 2 min. in water at 60° C. and 10 min. rest at room temperature retracted to condition V_4. . . where the length changed from 120 mm. to 21 mm., leaving a plastic elongation of 5%. Z_4
Third Experiment: The cyclical process of isothermal extension.				
Isothermal extension to fracture: Time: 3 min. Extension: 20 mm. to 120 mm., or		After this process, the parts of the strip immediately retract, so that after 10 min. the length has changed from 120 mm. to 30 mm., leaving a residual extension of 50%.		The rubber in condition Z_3 when allowed to retract further in water at 60° C., for 2 min. and for 10 min. at room temperature, undergoes a change from 30 mm. to 26 mm. leaving a plastic extension of 30%.

"Die Anisotropie des Kautschuks ist im Prinzip die thermodynamische Funktion des Valenzdifferentials der Schalenaggregation. Wenn in erster Instanz die Anisotropie des Kautschuks eine Differenzierung der Valenzen der Polyprensphäroide nach innen zur Voraussetzung und eine reziproke Differenzierung des Valenzdifferentials nach aussen zur Folge hat, so resultiert in zweiter Instanz aus einer weitergehenden thermischen Differenzierung der Valenzen eine reziproke Differenzierung der Anisotropie. Das ist

der Joule-Effekt. Er ist gleichzeitig eine reversiblen Verschiebung einer dispersen Kristallisation, verbunden mit reversiblen Wärme- und Dichteänderungen und einer reversiblen Verschiebung von Lichtreaktionen . . . Und nochmals die anisotrope Aggregation. Man kann sagen, das Valenzdifferential der isotropen Aggregation wird differenziert durch die thermodynamischen Faktoren der anisotropen Aggregation . . ."

Calorimetric Experiments in Connection with the Gough-Joule Effect, and their Theoretical Explanation

Definition and Experimental Determination of the Heat of Elongation. A knowledge of the heat which is produced and absorbed in the elongation and retraction of the rubber is of prime importance in a thermodynamic discussion of the Gough-Joule effect. It must not be expected that the magnitude of this heat effect will represent a constant of the material which can be definitely determined, like the melting point of a crystalline substance. Rather this magnitude is like the other "constants" of rubber in that it depends to a high degree upon the kind of rubber used and on the age, previous treatment, and temperature of the particular sample upon which the measurement is made. Nevertheless, the determination of the order of magnitude of this heat of elongation is of great interest for the sake of comparing it with the maximum work involved in the process of elongation. By measuring these two quantities under comparable conditions on the same rubber test specimen, the comparison can be made without the introduction of disturbing variables.

The first quantitative determination of the heat of elongation of rubber was made by Hock and Bostroem.[132] First of all, it is important to make clear just what is the nature of the measured magnitude. If the heat per gram of rubber which is given off during a more or less rapid elongation is measured, it must be supposed that at the same time a certain amount of frictional heat is set free. Besides, in the early stages of the elongation there is a slight cooling, as was shown by the observations reported by Joule.[133] This cooling is similar to that observed in the elastic stressing of other materials than rubber, such as metal wires. The cooling of metal wires by tension has also been determined by Joule, and more accurately by Edlund.[134] The measurements of this latter investigator are in agreement with the requirements of thermodynamics.

It is therefore to be expected that the determination of the heat of elongation will give a rather complex magnitude. However, only that quantity of energy which is deposited in the rubber structure in a latent and reversible form is to be considered as the equivalent of the cohesive forces which come into play in the transition of the rubber into the anisotropic form. That alone is suitable for explaining the relationship between increasing alignment of the colloidal micelles and the associated increase in density and production of heat.

Fundamentally therefore, the problem was not to subject the process of elongation to thermal measurement, but rather to determine the difference in the energy contents in the isotropic and the anisotropic states.

[132] See p. 437 of this book and *Z. Elektrochem.*, **31**, 409 (1925).

[133] See p. 415 of this book; also L. Hock and S. Bostroem, *Kautschuk*, **2**, 131, (1926).

[134] *Pogg. Ann.*, **126**, 539 (1865); see also O. D. Chwolson, "Lehrbuch der Physik." Vol. 3, p. 565, Braunschweig, **1905**; Müller-Pouillet, "Lehrbuch der Physik," Vol. 3, p. 1; and "Thermodynamik," by A. Eucken, pp. 114 and 448, Braunschweig, **1926**.

In order to obtain a preliminary conception of the order of magnitude of the Joule heat, Hock and Bostroem allowed a piece of elongated and hardened raw rubber (a strip of sheet elongated to about 600 per cent) to relax in a water calorimeter at about 27° C. From the measured cooling of the contents of the calorimeter they obtained a latent heat of the order of magnitude of 10 calories per gram of the rubber used.

Even this first approximate determination showed that the heat of elongation greatly exceeds the energy utilized in the elongation, which is of the order of magnitude of one-tenth calorie per gram of raw rubber. (The heat of elongation might more exactly be referred to as the heat of transformation into the anisotropic state, "Anisotropierungswärme," or with the opposite sign as the heat of transition into the isotropic state, "Isotropierungswärme," if it is desired to avoid the expressions "heat of solidification" and "heat of fusion.") The frictional heat produced with the work of elongation must therefore amount to a negligibly small fraction of the reversible heat quantity involved. It need not be considered, therefore, since it is smaller than the error that will be made in the determination of the latent heat due to the intrinsic uncertainty concerning any rubber sample.

The complex nature of the Joule heat is therefore very obvious from a theoretical point of view, but it is of little significance in a practical way. Accordingly, it appears that it would be possible to determine the Joule heat directly from the elongation or relaxation process as well as from the energy difference between the isotropic and anisotropic states. However, measurements of this sort made by Hock and Bostroem following Joule's method did not lead to satisfactory results, and showed only that the heat given off was roughly proportional to the amount of elongation.[135] By means of a multiple thermocouple with the junctions embedded in a rubber strip, the temperature rise which accompanied the elongation of the strip was measured. The specific heat of the rubber at the same temperature (about 17° C.) was measured calorimetrically in an indirect manner, the average value obtained being 0.38 calories per gram per degree Centigrade. This determination of the specific heat was not very exact, and the inexactness could not be attributed exclusively to the indirect method of measurement. The quantity of heat calculated from the specific heat and the rise in temperature did not agree very well with the heat of elongation as determined by other methods described below. (*See* p. 441.)

The best method for determining the latent heat of elongation proved to be a method based on a cyclic process. The heat of swelling in a solvent such as benzene or benzine is measured, both for isotropic raw rubber and for rubber that has been elongated and hardened in an anisotropic state. In both cases the rubber reaches the same final state, so that the difference in the heats of swelling for the two forms is therefore equal to the heat of transformation. In this manner Hock and Bostroem[136] have determined the latent heat of elongation as a function of the degree of elongation. For that purpose a sensitive differential calorimeter was used. This calorimeter consisted of two gold plated beakers which were surrounded on all sides with water or with an air jacket, which in turn was contained in a metal vessel. The outer vessel of tin was as thoroughly insulated with paper as was pos-

[135] See S. Bostroem, Dissertation, Giessen, *Kolloidchem. Beihefte*, **26**, 459 (1928).

[136] *Gummi-Ztg.*, **41**, 1112 (1926). Also L. Hock, *Kautschuk*, **3**, 337 (1927), and the above-cited dissertation of S. Bostroem. The complex nature of the heat of swelling here observed need not be considered. (See also p. 478.)

sible. A copper-constantan thermopile consisting of forty couples was used with a mirror galvanometer to measure the temperature difference between the two vessels. In each Weinhold flask there was a tin-plated vessel provided with a valve. The rubber, either isotropic or anisotropic, was placed in the one, while the other was left empty. When the valve was opened from the outside, the calorimeter fluid flowed in and swelled the rubber.[137] The swelling of the isotropic rubber showed an absorption of heat which amounted to from 0.1 to 5 calories per gram when benzine was used as the solvent, the amount of heat being dependent upon the kind of rubber used and upon the age of the rubber. The swelling of anisotropic rubber showed a cooling which was more marked the greater the elongation. The rubber, both isotropic and anisotropic, was used in the form of small pieces which were mixed with metal pieces for the sake of better thermal conductivity. The amount of heat absorbed was determined after each separate experiment by an electrical calibration of the calorimeter in which a corresponding temperature change was produced by electrical heating in the same time interval. Both kinds of rubber came to practically the same final state in a comparatively short time. For the swelling of the isotropic form, the rubber was temporarily stretched to a corresponding elongation and relaxed before the measurement was made on it. This was done as an added precaution to make sure that the calorimetric measurement involved practically nothing but latent heat.

The Heat of Elongation as a Function of the Degree of Elongation. The results of the measurements made by Bostroem can be shown in the form of a graph. The latent heat, the increase in which may be predicted from theory on the basis of the orientation[138] and close packing of the particles, increases as a linear function of the amount of elongation. Since the work performed during the elongation, when expressed in thermal units, is vanishingly small as compared to the liberated heat, the heat of transformation which is measured in the calorimeter without the performance of external work is practically the same as the change in the total energy of the system when it changes from one state to the other. The error involved is within the reasonable limit of error of the experiment.[139]

In Table 9 are given the corresponding values of elongation (in per cent) and heat of elongation (in gram calories per gram of raw rubber). Experiments with rubber at still higher elongations are planned by the author and his collaborators.

TABLE 9.—*The Dependence of the Latent Heat of Elongation on the Degree of Elongation.* (*According to Hock and Bostroem.*)

Elongation per cent	Heat of Elongation in g. cal. per g. of Rubber
186	0.84
361	2.33
428	2.86
621	4.58
658	5.24
821	6.80

[137] In regard to improvements in the technique of the experiment, see Fr. Hartner, Dissertation, Giessen, **1929.** (*See* pp. 463 and 478.)

[138] See *Z. Elektrochem.*, **31**, 407 (footnote) (1925); also p. 446 of this book, where a further proof of the theory is furnished by x-ray measurements.

[139] In regard to the definition of the thermodynamic values here encountered, see J. Eggert, "Lehrbuch der physikalischen Chemie auf elementarer Grundlage" 2nd Edition, edited mutually with L. Hock, p. 26 ff., S. Hirzel, Leipzig, **1928.**

The remarkable fact that there is no appreciable quantity of heat involved at elongations of 100 per cent or less is shown in Figure 76. Perhaps this fact is related to the change in sign of the thermal effect for the smaller elongations. It may be that for elongations of 100 per cent or less, the normal thermodynamic effect and the effect which is conditioned by the beginning of the anisotropy compensate each other. Incidentally, it is at 100 per cent elongation that the x-ray interference pattern first attains appreciable intensity. This fact, which was first pointed out by J. R. Katz, is discussed again on p. 445.

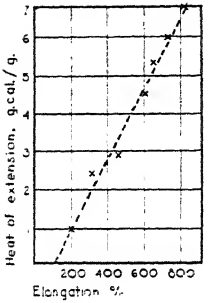

Figure 76—Heat of extension of raw rubber: its dependence on the degree of extension. (According to L. Hock and S. Bostroem.)

Theoretical Explanation of the Heat of Elongation. If the measured heat of elongation is compared to the energy employed in producing the elongation (which latter can be measured directly in kilogram-meters by means of a Schopper "bending" balance) it will be found that the energy used is only a small fraction of the latent Joule heat. For average elongations this fraction is about 2 per cent. As has already been pointed out, that fact makes it impossible to consider the Joule heat as being of the nature of frictional heat. Rather it undoubtedly must arise from the mobilization of some molecular forces such as the van der Waal forces. Possibly the elongation of rubber may be compared to the condensation of water vapor to liquid water in this respect. There is also a certain amount of volume energy ($pv = RT$ per mol) employed in compressing the gas at the pressure of the saturated vapor. This energy is likewise quite trivial in comparison with the important latent heat which enters into the phenomenon. This latent heat is produced by the molecular forces that come into action when the condensation occurs. In a similar manner, the occurrence of the Gough-Joule effect in raw rubber is connected with a packing together of the structure (and in particular with an alignment of the rod-like molecules). Accordingly, a volume energy is also involved here (as has been previously mentioned, the density of rubber increases by several per cent when the rubber is elongated). This energy which is utilized is therefore contained in the work of elongation. To be sure, the exact nature of the molecular forces in rubber is unknown, so that the work of compression unfortunately cannot be calculated by theory. If for each stage of the elongation there is a functional relation (of unknown form) between the applied force k and the volume decrement, the work reversibly stored up in the structure of anisotropic rubber may be expressed by

$$A = \int_{v_2}^{v_1} k \, dv$$

Application of the Second Law of Thermodynamics to the Elongation Process. Unfortunately, the maximum work (reversible in the ideal thermodynamical sense) cannot be directly determined. The work which is actually used up in the elongation process, which can easily be measured from a stress-strain curve by means of a planimeter, is doubtless of a complex nature. Aside from the ideal work associated with the change in volume, there is always a considerable portion of frictional work included and also work which is utilized in permanently changing the form of the rubber, since it is not possible to carry the rubber through an isothermal, and at the same time a completely reversible cycle.

Nevertheless Hock and Bostroem have attempted to test the validity of the Gibbs-Helmholtz equation as applied to rubber, since it is applicable to ideal processes of this kind. It was thought possible at least to find wherein lay the difficulty of such a task. Letting A stand for the maximum work performed by the system, U the decrease in its total energy and T the absolute temperature, we have the relation

$$A - U = T \frac{dA}{dT} \qquad (24)$$

which is the Gibbs-Helmholtz equation. If A, U, and T are known from mechanical and calorimetric measurements, the temperature coefficient of the maximum work, i.e., its change per 1° C., can be predicted. If the experimental value is found to be in agreement with the theoretical, the equation will be confirmed, and the requirements of the first and second laws of thermodynamics will evidently be fulfilled by the system. Since the work of elongation as measured does not possess the characteristics of a maximal work, the equation must be considered as incompletely satisfied. The size of the temperature coefficient of the free energy can be estimated, however, by substituting the known values of A, U and T in the above equation. The work performed by the system is to be taken with a positive sign, and a decrease in the total energy is also to be considered positive. For an elongation process referred to 1 gram of rubber and an elongation of 658 per cent, U has a value of 5.24 calories, while according to the above-mentioned measurement of Hock and Bostroem, the corresponding value of A is about — 0.2 at a temperature of 290° K. The ideal value of A would be less than this, but its exact magnitude is of small importance, since, within the limits of error in the value of U we may replace $-U$ with $A-U$. Accordingly, in this approximate calculation we have the value of approximately + 5 on the left side of equation (24) and 290 dA/dT on the right side. The temperature coefficient of the maximum work therefore comes out to be

$$\frac{dA}{dT} = \frac{+5}{290} = +0.017$$

According to this, the ideal reversible work of elongation must increase by 0.017 calories for each degree of temperature increase. Actually, it is well known that a quite marked decrease in the work of elongation is observed with an increase in temperature.* Thus a negative temperature coefficient exists instead of the positive coefficient which might be expected from the above conclusions as well as from kinetic considerations. Apparently, the work which is actually measured must include a considerable portion of irreversible frictional work, and work which is absorbed in permanent altera-

* See Translator's Note on p. 408 for criticism of this interpretation.

tion of the shape. Without doubt, such work would have a negative temperature coefficient of some magnitude, which would give a negative coefficient to the total work.[140] If it were possible to eliminate the irreversible portion of the work it is naturally to be expected that the Helmholtz equation would be satisfied.[141]

It may be supposed that the work involved in the retraction of raw rubber could be measured by changing the velocity, which would change the proportion of friction. By extrapolating to zero velocity, it might then be possible to estimate the amount of the frictional work. By that means it might be possible to determine the correct temperature coefficient, at least in regard to sign. To be sure the elongation velocity must not be made too small, because then a completely new stress-free molecular structure of the rubber may be produced by a process of internal slippage. It is a well-known fact that when raw rubber remains distorted for some time at room temperature or at a higher temperature, it finally ceases to show any resisting tension. The anisotropic structure goes over into an isotropic structure by internal slippage while the external deformation is kept the same. Moreover, the raw rubber that had been racked to 10,000 per cent and then relaxed with a resulting permanent set of 1,000 per cent (as described by Feuchter) did not show any remaining anisotropy, according to x-ray measurements by E. A. Hauser. (*See* p. 449.)

Relation Between Heat of Elongation and X-ray Interference. Hauser, in some work which will be discussed in more detail later, has recently studied the process of extremely slow elongation. He found that when the elongation was slow the x-ray interference and the occurrence of noticeable anisotropy were almost totally absent. He also found that neither the Joule heat of elongation nor the change in density was noticeable. Both discoveries are in the best of agreement with the theory of the Joule effect proposed by Hock. In that theory, the heat which appears is explained as being the heat of the transformation into an anisotropic state. If the isotropy is maintained, no heat would be expected.[142] In order to investigate this relationship more closely, Hauser and Rosbaud secured elongation curves for raw rubber at various velocities and at various temperatures. By simultaneous observation of the x-ray interference and of the thermal behavior, they showed that both the intensity of the interference spots and the quantity of heat involved in the process are proportional to the amount of elongation only when the rate of elongation is kept constant. It would, therefore, be more exact to speak of the proportionality between the quantity of heat involved and the anisotropy,

[140] By way of comparison, it may be stated that rapeseed oil, for example, exhibits the considerable temperature coefficient of 12 per cent with respect to its internal friction. On the basis of the value + 0.017 for the temperature coefficient of maximal work and the value of 0.2 calories for the work utilized, the positive temperature coefficient of the ideal work of elongation of rubber amounts to about + 10 per cent. (The ideal reversible work forms only a portion of the work utilized and probably amounts to 0.1 calories or even less.) The temperature coefficient actually observed in this case amounts to about — 0.003 calories per degree or about — 1 per cent. It appears plausible that this slightly overcompensated neutralization may be attributed to a marked effect of the temperature upon the internal friction. That explanation involves the assumption that the temperature coefficient of the internal friction for rubber between 17° and 31° C. is considerably larger [illegible] efficient for rapeseed oil.
[illegible] ier treatment of the
W.

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1929; also V. Bje
(1891).

[142] The writer had expected the absence of an in[illegible] because the phenomena of interference (anisotropy) are cau[illegible]
He is indebted to Messrs. Hauser
baud for the friendly confirmation of this
The inner connection among the three groups of phenomena constitutes the very basis of the theory of the Joule effect, which was first developed by the author in *Kolloid-Z.*, **35**, 40 (1924).

rather than between the quantity of heat and the elongation.[143] In this behavior is seen the effect of a flow phenomenon which is the more noticeable the more the velocity of flow exceeds the velocity of elongation at any temperature. In agreement with this, the highest degree of anisotropy can be produced only by the process of quick racking. An elongation curve for an extremely low rate of elongation (as obtained by Hauser and Rosbaud) [143a] is shown in Figure 77. By means of intermittent elongations and subsequent periods of flow, an elongation-flow curve can be obtained. If a line is drawn through the points representing the amount of flow of the test piece, the curve so obtained will represent a curve for a very low rate of elongation. (*See also* p. 449.)

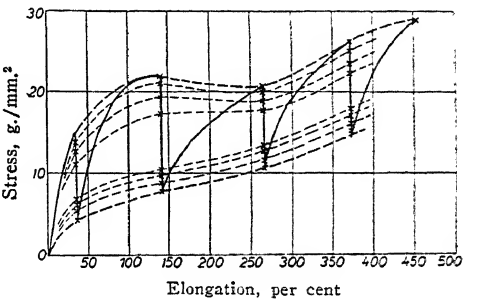


Figure 77—Cyclic extension curves for raw rubber.
(According to E. A. Hauser and P. Rosbaud.)
(Stress calculated on original section.)

The Temperature Function of the Heat Capacity of Rubber (Specific Heat). Important contributions to the knowledge of the thermal properties of rubber have been made recently by LeBlanc and Kröger [144] and by Ruhemann and Simon.[145] They have investigated the dependence of the specific heat on the temperature for various kinds of raw materials, which were studied under various conditions; i.e., normal, milled, elongated, frozen, etc. The agreement between the findings of the two groups of authors is not all that could be desired, to be sure. A complete picture cannot be obtained from the data available at present, but Simon and Ruhemann have attempted to give a critical explanation for certain outstanding points in regard to the behavior of the specific heat. Since they show in their figures the findings of LeBlanc and Kröger for comparison, use will be made of these figures in the present discussion, but the original work must be consulted in regard to details.

Simon and Ruhemann used a vacuum calorimeter to make their measurements, and investigated the specific heat of various samples of natural and synthetic rubber between — 100° and + 35° C. The thermal expansion and x-ray interference patterns were also studied in connection with these results. It was found that the gradual rise of the curve for the heat content was broken in various places by striking "anomalies." Three different anomalies were found in all. The first (designated as α) was in connection with the hardening of a phase of the rubber and was explained as being a general property of the amorphous state, since it showed a great similarity to the related phenomenon in glycerol and in other substances. In natural rubber, this anomaly is shown between — 80° and — 65° C. by a short, sharp rise in the

[143] See the formulation on pp. 436 and 446 in support of this idea, which had previously been advanced in the dissertation of S. Bostroem referred to there.

[143a] *Kautschuk*, **4**, 12 (1928).

[144] *Z. Elektrochem.*, **34**, 241 (1928).

[145] *Z. physik. Chem.* (Sect. A), **138**, 1 (1928).

curve of the heat capacity. This is shown for smoked sheets in Figure 78a, where the heat capacity per mol of isoprene is shown. In synthetic rubber this anomaly is shifted toward higher temperatures, as may be seen in Figures 78b and 78c, where the "jumps" occur at higher temperatures. The curve in Figure 78b is for synthetic H-rubber, while that in 78c is for W-rubber.

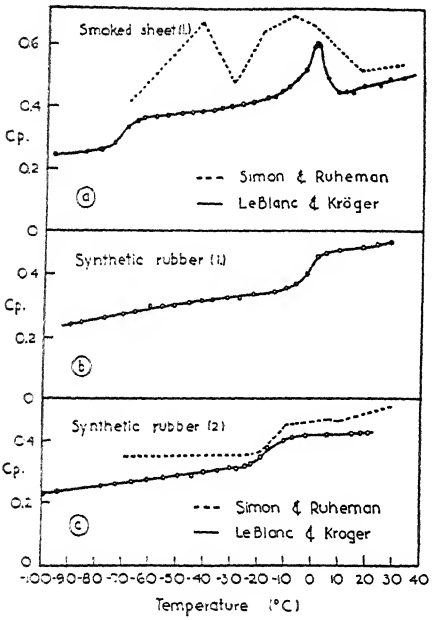


Figure 78—(a-c)—Specific heat of various types of rubber, as dependent on temperature.

(According to Simon and Ruheman and according to M. LeBlanc and M. Kröger.)

In natural rubber another anomaly, β, was observed in the neighborhood of 0° C., where the curve rises to a very prominent peak, as is shown in Figure 79. It is not probable that these anomalies are due to impurities contained in the rubber; rather they are to be ascribed to the rubber substance itself.

In the measurement of the specific heat of frozen sheets and frozen "cut sheets" the anomalies α and β were also found, although they were somewhat displaced on the temperature scale. In addition there was observed a third anomaly, γ, which was also found in racked rubber and which was explained as a "heat of fusion." These anomalies may be noted on Figures 80a and b. The energy content of this third anomaly, which occurs at approximately room temperature, amounts to about 4 calories per gram of rubber for sheet rubber and 6 calories per gram for "cut sheets." The occurrence of this anomaly is connected with the decrease in the opalescence of the rubber which takes place on heating, so that it appears to be altogether correct to refer to this anomaly as a heat of fusion. It is to be expected that a systematic continuation of the investigations along this line will contribute to a solution of the problem of rubber structure. In this connection should be mentioned an earlier observation by Stoll [146] that a thermal reaction occurs when rubber is massed at a temperature in the neighborhood of 60° to 80° C.

[146] *Gummi-Ztg.*, **40**, 1749 (1926); **42**, 745 (1928).

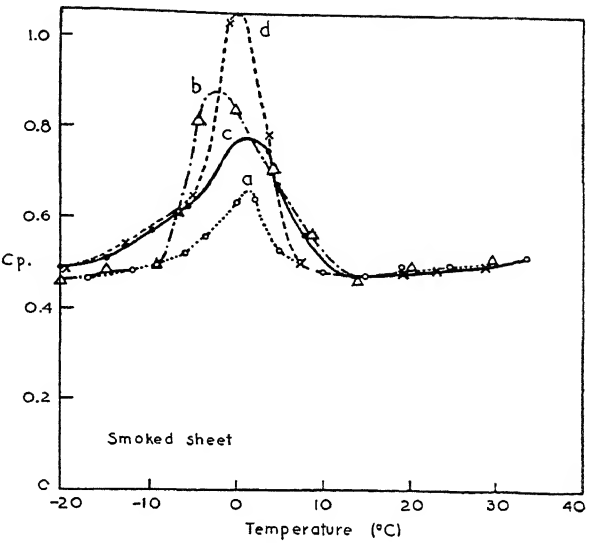


Figure 79—Variation of the specific heat with temperature for raw rubber in the neighborhood of 0° C.

(According to Simon and Ruhemann.)

a. 1st filling; suddenly cooled; 5 hours @ low temperature.

b. 2nd filling; suddenly cooled; 12 hours @ low temperature.

c. 2nd filling; evacuated @ 20° for 12 hours; then rapidly cooled; 1 hour at low temperature.

d. 2nd filling; held 1 hr. @ 40°; then slowly cooled; 1 hour at low temperature.

This reaction produces a marked decrease in temperature. It appears that there must therefore be in that temperature region another anomaly of the first kind mentioned above.

Recently A. van Rossem and J. Lotichius [147] have taken up the study of the freezing of rubber, and have studied among other things the relation between temperature and the density, hardness, and light absorption of raw rubber. This was done with the collaboration of J. R. Katz [148] in the domain

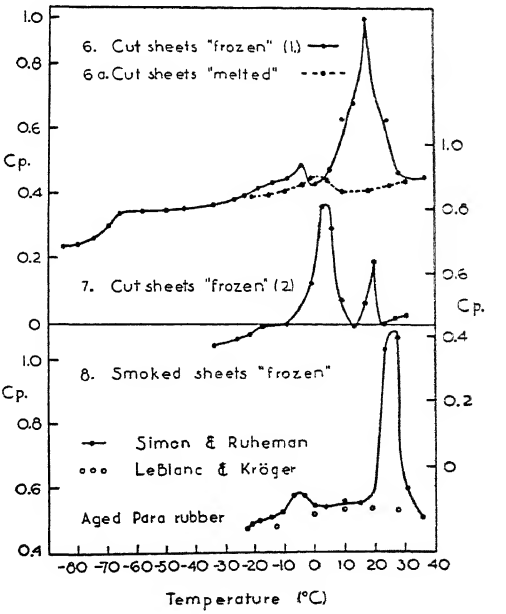


Figure 80—(a-b) — Variation of the specific heat with temperature for "frozen" rubber samples.

(According to Ruhemann and Simon and according to LeBlanc and Kröger.)

[147] *Kautschuk*, **5**, 2 (1929).

[148] *Z. angew. Chem.*, **38**, 439 (1925); *Kautschuk*, **5**, 6 (1929). See also E. A. Hauser and P. Rosbaud, "X-ray Studies on Rubber and Similar Substances," *Kautschuk*, **3**, 17 (1927). The crystal lattice of frozen rubber is found to be in agreement with that of elongated rubber.

of x-rays. All three of the above properties show a sharp decrease in their value at the same temperature, which is taken to be a manifestation of a fusion process. The above-mentioned authors also determined the "heat of fusion" of a sample of frozen rubber to be about 5 calories per gram. This determination was made in an ice calorimeter, employing the swelling process described above. The "melting point" rises when the rubber is stored for a period of a year or so, and inversely, new frozen rubber will thaw at a lower temperature than that which has been stored for a long time. In all cases, however, the same x-ray diffraction was observed. The original work must be consulted in regard to further detail. (*See also* p. 416.)

X-ray Investigations in Connection with the Gough-Joule Effect and Their Theoretical Explanation

Experiments of Katz. The theoretical explanation of the Gough-Joule effect, from the standpoint not only of the mechanical but also of the thermal and optical phenomena characterizing it, had led Hock to assume that stretched rubber had a fiber structure resulting from some particular interaction of adjacent forces. Macroscopic proof of this fiber structure was later offered by his cleavage experiment.[149] With H. Stintzing he evolved the plan of proving this fiber structure by means of x-ray photographs also.[150] For extraneous reasons, the experimental work in connection with the investigation was delayed, and J. R. Katz [151] actually made the first observations on the occurrence of x-ray interference in the case of stretched rubber.

By means of these x-ray experiments, the ordered structure of stretched rubber was proved visually for the first time. The determination amounted only to an observation of a lattice spacing (Identitätsperiode) in the direction of stretch, and it remained doubtful to what extent it was correct to speak of the temperature of thermal relaxation as the "melting point" (Hock, 1924). Nevertheless, in spite of the surprising analogy between these observations and those of the melting of a crystallized material (collapse of the lattice structure, disappearance of the x-ray interferences, thermal phenomena), the exact proof that the heat of stretching was identical with a real "heat of crystallization" (Katz, 1925) was still lacking. In any case, from the beginning, as previously shown (p. 420), this heat was considered to be analogous to the Joule-Thomson effect in real gases (heating during compression, cooling during expansion). According to the kinetic method of presentation by the author, it was conceived as a latent heat proceeding from the agency of a van der Waal's cohesive force, and may be spoken of for the moment as a heat of crystallization, in which these forces must be considered as lattice forces. The more extensive, quantitative measurements of E. A. Hauser and H. Mark (1926), and more particularly those of H. Mark and G. von Susich (1928), first led to the justification of this concept. However, the stability of form (!) of unstretched rubber admits no remnant of similarity with the relaxation of the process of melting (*see* p. 456), so that the author must still prefer the expression "a kind of melting point."

Scherrer had experimented earlier with unstretched rubber using x-rays and had found that it was very similar to gelatin. The x-ray diagram showed the typical characteristics of an amorphous substance, and induced Scherrer

[149] See Fig. 73 on p. 422 of this book.
[150] *Kolloid-Z.*, **35**, 40 (1924).
[151] *Chem.-Ztg.*, **49**, 353 (1925); *Naturwissenschaften*, **13**, 410 (1925); *Kolloid-Z.*, **36**, 300 (1925); *ibid.*, **37**, 19 (1925); Katz and Bing, *Z. angew. Chem.*, **38**, 439 (1925).

.. come to the conclusion that both substances might be composed of a mix-ture of two amorphous materials.[152] * †

It is only with the extension of rubber that the picture changes. Instead of merely the wide "amorphous ring" which is observed when a strip of unstretched rubber one millimeter thick is irradiated with x-radiation from a copper source and a photographic plate is placed behind it and perpendicular to the impinging primary ray, there appear in the study of threads of rubber stretched three or more times their normal length, phenomena which remind one of a crystal interference pattern. Next to the persisting "amorphous ring" are to be found dot-like interference spots, as they appear characteristically in substances which are composed of many small crystals all lying parallel to some crystallographic direction, in this case to the direction of stretch. At all events, a certain degree of extension must first be reached before these interferences appear, and this minimum is about 100 per cent. The greater the extension, the greater is the intensity of the interference points as compared with that of the amorphous ring, which latter, however, always remains distinguishable, regardless of the degree of extension. These same interference patterns may be seen in the case of torsion of a rubber strand as well. They provide a further proof of the anistropy of rubber, and justify immediately the question as to whether rubber may perhaps exist in crystallized form. Undoubtedly, unstretched rubber is in an amorphous form. It is certainly reasonable to assume the existence in it of molecules or quasi-molecules imagined to be of oblong form and existing next to each other in lawless disorder. The kind of crystal structure which is indicated by x-ray investigations is not essentially present in rubber, but is due to the process of stretching, a fact which Katz had already emphatically pointed out in his first publication. From the standpoint of pure chemical investigation also, the existence of extended chains of molecules has been predicted (Staudinger, 1924).

Anisotropy is directly associated with the parallelism and close packing of the molecules or molecular aggregates. In order to ascertain to what degree the Gough-Joule heat might properly be considered as a heat of production of anisotropy, L. Hock and H. Stintzing undertook the problem of determining the degree of parallelism of the micelles by means of x-rays, and of determining the relation between this degree of parallelism and the heat effect observed during the extension process.[153] Thus finally the problem became one of stating the heat effect not with reference to the unit weight of the aggregate which in general takes part in the process of extension, but only to the mass which actually participates in the production of anisotropy. If

[152] *Cf.* R. Zsigmondy, "Kolloidchemie," section by P. Scherrer, 4th ed., p. 409, Otto Spanner, Leipzig, **1922**. Here complete information concerning the experimental method is given. Later, G. L. Clark, in the United States, used x-rays in the study of rubber; see *Am. J. Roentgenol. Radium Therapy*, **12**, 556 (1924). In this reference, balata and gutta-percha are also discussed. (Clark & Bergman.) See also Hauser & Rosbaud, *Kautschuk*, **3**, 17 (1927) and also **3**, 228 (1927), and finally F. Kirchhof (Gutta-percha), *Kautschuk*, **5**, 175 (1929); Dissertation, Hanover, **1929**.

* Translator's Note. Reviews of the early studies of the composition and structure of rubber have been written by Hauser and Bary, *Rubber Age (N. Y.)*, **23**, 685-8 (1928) and by G. L. Clark, *India Rubber World*, **79**, (5) 55-59 (1929).—N. J.

† Translator's Note. One of the earliest writers to mention rubber as being of a two phase nature was Govi, *Les Mondes*, **19**, 640 (1869). His assumption that rubber was similar to a solid foam was later disproven by Thomas, *Les Mondes*, **20**, 7 (1869) and by Hesehus, *J. Russ. Phys. Chem. Soc.*, **14**, 320 (1883). Various other authors have advanced theories concerning the structure of rubber on the assumption of a two-constituent system: Mallock, *Proc. Roy. Soc. (London)*, **46**, 233 (1889); Chaveau, *Compt. rend.*, **128**, 388, 479 (1889); Fessenden, *Science*, **20**, 48 (1892); Breuil, *Caoutchouc & gutta-percha*, (1904-5); Schwarz and Kemp, *Caoutchouc & gutta-percha*, **8**, 5293 (1911); Cheneveau and Heim, *Compt. rend.*, **152**, 320 (1921); Bary and Fleurent, *Compt. rend.*, **184**, 947 (1927); *Rev. gén. caoutchouc*, **4**, (31) 3 (1927).—N. J.

[153] See L. Hock, *Z. Elektrochem.*, **31**, 404 (1925).

one further assumes that the rubber which Feuchter racked to a 10,000 per cent extension, and which was no longer capable of swelling, had to a certain approximation reached its full degree of anisotropy,[154] then there becomes necessary for the determination of the above magnitude only the determination of its heat of relaxation. This work has been planned by the author.

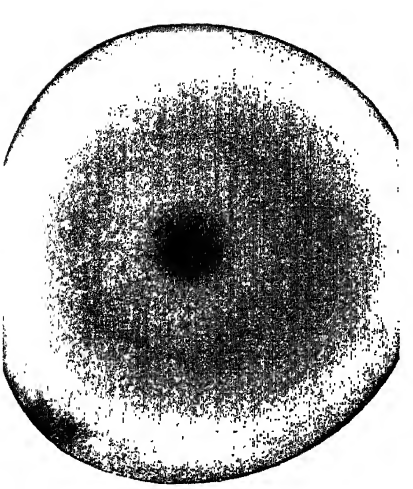
Experiments of Hauser and Mark. On account of the above-mentioned delay in the preparation for these experiments, the investigation of the interrelation of the intensity of the interference spots and the degree of extension of the rubber was meanwhile undertaken by Hauser and Mark,[155] who published the first exhaustive and extensive quantitative study of the structure of stretched samples of rubber. Their research also dealt particularly with the question as to whether the aspect of the interference pattern remains unaltered during continued extension, during which its intensity increases, or whether this aspect is dependent on the degree of extension. Only in case this pattern remains unchanged during continued extension can we agree on a definite similarity to a crystalline structure, which is distinguished by the property of fixed lattice spacings. With their mastery of the experimental method and of the theoretical interpretation of difficult x-ray diagrams attained in the Mark laboratory, these authors succeeded to a great extent in making the crystalline nature of stretched rubber evident, as a result of their extensive measurements and calculations.

With this object in mind, diagrams were obtained using a film of dried latex, which had been subjected to extensions as high as 700 per cent. In this experiment, the interferences first became evident at an extension of about 80 per cent and with further extension increased in intensity. A careful measurement of these photographs showed that all interference spots occupied a position which was, within 0.5 per cent, independent of the degree of extension. Concurrent photometric experiments showed a linear dependence of the intensity of the interference spots on the degree of stretch (not of tension), which is equivalent to an increase in the number of directed particles.

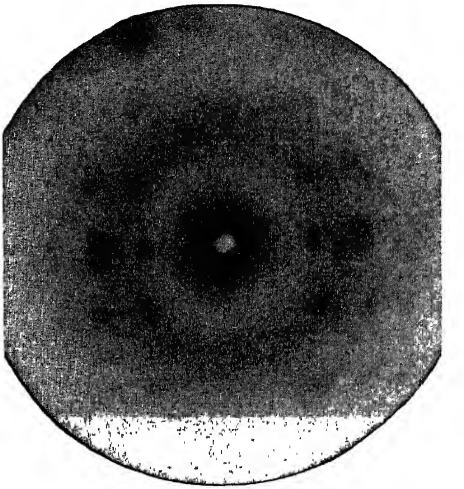
It must be remembered that in view of the discoveries of Hock and Bostroem, the same linear relation between the heat effect and the degree of extension exists, and thus the parallelism of both phenomena leads immediately to the interpretation which follows. As the number of directed particles increases with increasing extension, so also the mobilization of van der Waal's forces (inter-micellar forces) between the directed and closely packed complexes advances, these forces being causally related to the parallel positions of the particles (micelles) and becoming evident in the characteristic variations of the latent heat. Even as the interference patterns first become evident at approximately 100 per cent extension, so also as a parallel phenomenon, an appreciable heat effect first becomes evident at about the same extension. The heat effect, which is related to the Gough-Joule effect, is, therefore, also in causal relationship to the x-ray interference patterns. If these patterns are absent, as with the phenomena of flow, (mentioned in the previous section as being slow and as occurring without change in density) then there is no cause for the appearance of a heat of anisotropy. With this, there is possible a strong confirmation of the theory advanced by the author, namely, that the

[154] *Cf.* p. 432, as well as the footnote regarding the exhaustion of the micellar forces in the case of extremely stretched rubber.

[155] *Kolloidchem. Beihefte*, **22**, 63; **23**, 64 (1926). The relation between the heat effect and the degree of extension has already been discussed in a previous section.

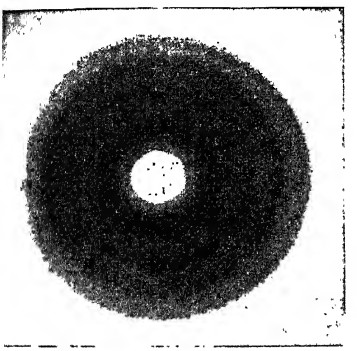


Unstretched

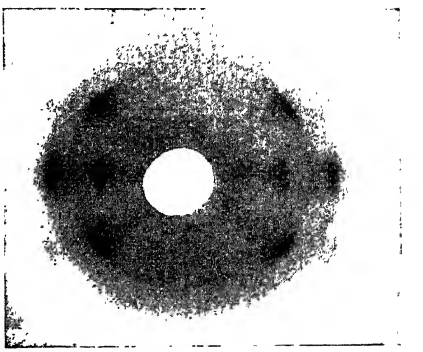


Stretched 500 per cent

Figures 81 and 82—X-ray diagrams of raw rubber.
These figures are the first diagrams made by J. R. Katz
[*Naturwissenschaften*, **13**, 414 (1924)].



Unstretched



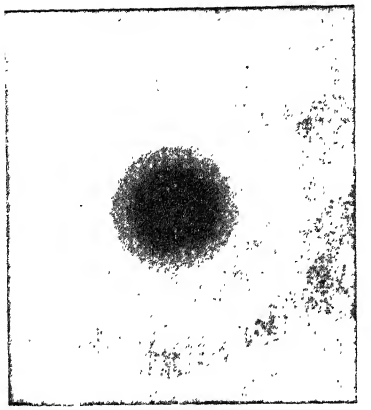
Stretched

Figures 83 and 84—X-ray diagrams of frozen rubber.
(According to M. Hünemörder and P. Rosbaud.)

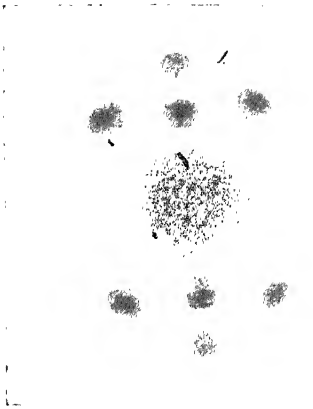
Gough-Joule heat of extension increases in proportion to the number of parallel and closely packed particles. (*See* p. 438.)

In Figures 81 to 87 again, a number of typical Debye-Scherrer x-ray diagrams are presented. There is a diagram of unstretched and stretched rubber from the first publications of Katz;[155a] next, from the experiments of Hünemörder and Rosbaud[156] a diagram of unstretched and stretched "frozen" rubber (Figs. 83, 84), and later a diagram (Fig. 85) by the same authors, of very slowly stretched smoked sheet, which was, therefore, isotropic under flow at 500 per cent extension. This sample gave scarcely any discernible interference pattern, while under rapid extension the same material gave a marked fiber diagram (Fig. 86). Finally, Fig. 87 shows the diagram obtained by H. Feuchter, noteworthy because of even stronger and

[155a] *Naturwissenschaften*, **13**, 410 (1925). [156] *Kautschuk*, **3**, 229 (1927).



Slow Elongation



Rapid Elongation

Figures 85 and 86—X-ray diagrams of smoked sheets stretched to a 500 per cent elongation.
(According to E. A. Hauser and P. Rosbaud.)

sharper crystal interferences. This is a picture of rubber under maximum racking, in which the "amorphous ring" is hardly apparent. Let it be here stated that diagrams similar to those of rubber are obtainable from balata and gutta-percha in the stretched state. Communications from Hauser[157] and his collaborators concerning these materials are before the authors. In the United States, G. L. Clark,[158] in particular, has undertaken similar problems.

Returning to the details of the experiments carried out by Hauser and Mark concerning the structure of stretched rubber samples, it becomes of importance to draw conclusions from the quantitative evaluation of the diagrams produced, as to the nature of the molecular structure thus suggested. Of primary importance is the inference that it necessarily follows from the increase in number of the crystallized phases that new individual crystals are produced by new nuclei, and not that the old crystallites, already present, grow further. While the intensity of the interference dots increases in proportion to the extension, (within limits of 25 to 30 per cent) the intensity of the "amorphous ring" suffers a linear decrease with increasing extension of the rubber.

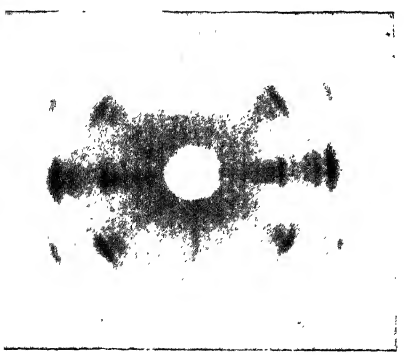


Figure 87—X-ray diagram of "racked" smoked sheets at an extension of about 9,000 per cent.
(According to E. A. Hauser.)

[157] *Kautschuk*, **3**, 17, 228 (1927). Acknowledgment is here given Dr. Hauser for the kind loan of the original pictures for the preparation of the above Figures.
[158] *Ind. Eng. Chem.*, **18**, 1131 (1926); *India Rubber World*, **79**, (5) 55 (1929).

Although the position of the spots is independent of the elongation,* the per cent elongation at which the various spots become prominent depends largely on the rate of extension, as shown by Hauser and Mark, *Kautschuk*, **3**, 228 (1927). The fibrous structure as indicated by the interference spots, is formed at much lower elongations if the rate of elongation is high. This subject of the dependence of the fibrous state on the rate of elongation has been studied by Acken, Singer and Davey, *Ind. Eng. Chem.*, **24**, 34 (1932), and also *Rubber Chem. Tech.*, **5**, 30 (1932). To quote from their abstract. "It is shown by x-ray diffraction methods that a time interval is required to build up a fiber structure in stretched rubber . . . The most probable explanation seems to be that time is required either to squeeze out unfavorably oriented molecules to the interfaces of fibers made up of favorably oriented molecules; or to pull out in the direction of fiber orientation, tangled portions of molecules. Such a picture would cause the easily stretched, favorably oriented molecules to assume the role usually played by the more solid phase of a gel, and would cause the less favorably oriented molecules (or portions of molecules) to play the part ordinarily played by the liquid phase of a gel."

The lattice spacing along the axis lying parallel to the direction of extension may be measured directly from the diagrams taken with copper radiation using the relation ("Schichtlinienbeziehung") of Pólányi.[159] An average value of 8.1 Å is determined for this lattice spacing.

The arrangement of the interference dots may be explained by the hypothesis that during extension a crystallized phase is produced, which is oriented in a direction with one axis parallel to the direction of stretch. From the position of the individually observed interference dots, as well as from the relation of their respective intensities, the symmetry of the unit cell may be calculated by the rules of x-ray spectral structure determinations. In reality, one observes considerably fewer interference dots than should be expected for a supposed structure, and for this reason there exist quite serious uncertainties as to the interpretation of the diagrams, inasmuch as the indexing of the individual points is possible only with the help of certain assumptions. Nevertheless, Hauser and Mark, in the publication mentioned, have already come to the conclusion that the unit cell of stretched rubber can be assigned to the rhombic crystalline system. Inasmuch as both Mark and G. von Susich[160] had been successful in experimentally determining the lattice spacing not only in the direction of the fiber axis, but also in the two other elementary directions, the interpretation of the diagram has become considerably more reliable. As a result of this work, the symmetry of the unit cell appears to be rhombic.

Inasmuch as we will consider more closely the results obtained by Mark and G. von Susich, and use the further conclusions at which K. H. Meyer and H. Mark[161] arrived, let us next describe without too much detail the experimental method used by these investigators.

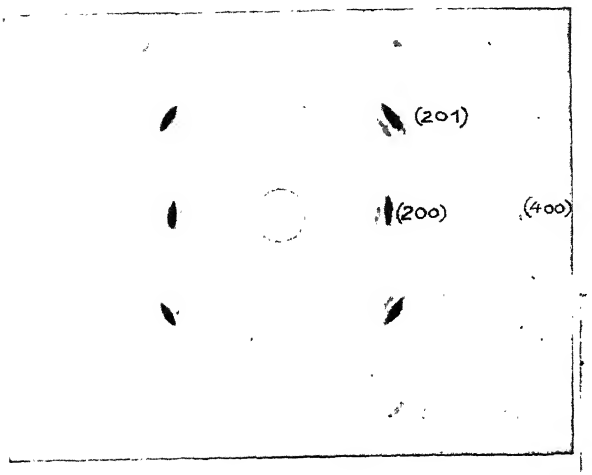
Von Susich's experiments gave diagrams with a greater number of definite interference spots, which allowed conclusions to be drawn on a much more detailed orientation of the micelles, than was possible from the earlier diagrams of other experimenters. This was particularly true in the case of very thin rubber films, at the great elongation of about 1,000 per cent. In this

* Translator's Note by N. J.

[159] *Z. Physik*, **7**, 149 (1921).

[160] *Kolloid-Z.*, **46**, 11 (1928). In recognition of the importance of this work which appeared after the manuscript of this contribution to the present text had gone to press, the author resolved to strike out the text as first planned —based on the older work—and to substitute in the otherwise unaltered continuity of the whole the developments described below. However, from this new work was taken the above-mentioned, corrected value (8.1 Å) for the lattice spacing in the direction of stretch. Hauser and Mark earlier gave the value 7.68 Å. *Cf.* further G. L. Clark, "Applied X-rays," McGraw-Hill Book Co., New York, 1932, also, *Ind. Eng. Chem.*, **18**, 1131 (1926).

[161] *Ber.*, **61**, 1939 (1928). *Cf.* also the concise introduction to the theory of the principal valence chains, especially applied to the chemistry of cellulose by K. H. Meyer, *Z. angew. Chem.*, **41**, 935 (1928) and also Meyer and Mark, *Ber.*, **61**, 607 (1928). A discussion of the purely chemical problem, which at present is still hotly disputed, naturally does not come into question at this point. See pp. 169 ff.



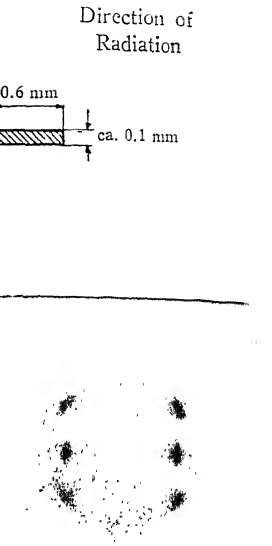
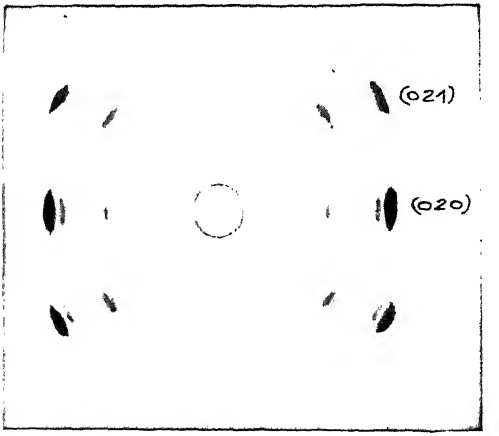


Figure 88—Schematic X-ray diagram.

Figure 89—Actual X-ray diagram. Irradiation perpendicular to the plane of the rubber film. Sequence of intensities: (200) (201).



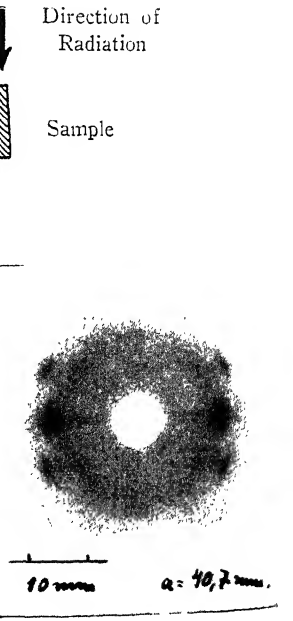


Figure 90—Schematic X-ray diagram.

Figure 91—Actual X-ray diagram. Irradiation parallel to the plane of the rubber film. Sequence of intensities: (020) (021).

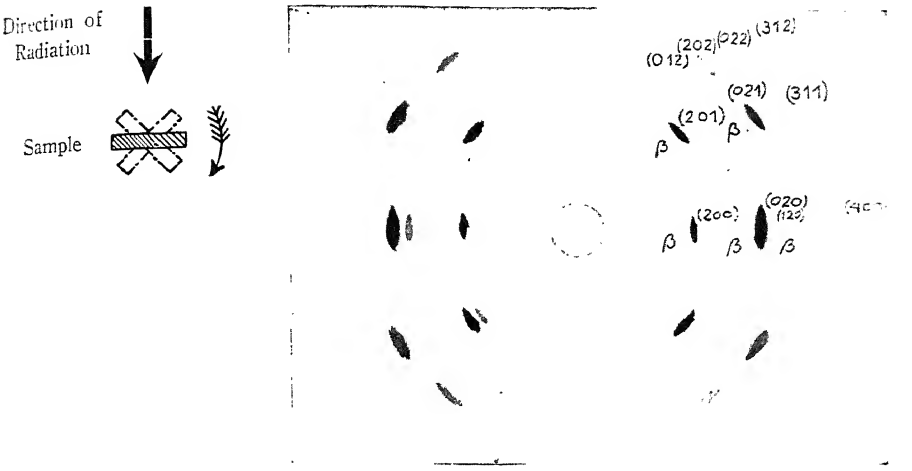


Figure 92—Schematic X-ray diagram.

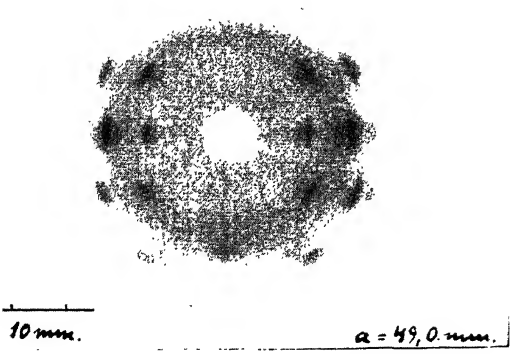


Figure 93—Actual X-ray diagram.

During irradiation of a rubber film rotated about an axis parallel to the direction of extension. Sequence of intensities: (020) (200) (201) (021).

Figures 88 to 93—Schematic and actual X-ray diagrams of greatly stretched thin rubber films (according to H. Mark and G. von Susich).

manner it was possible to calculate reliably the lengths of the other two edges of the lattice, and thus to undertake a certain indexing of the individual interference spots, since henceforth the orientation of the crystalline rubber micelles occurs not only in the one, but also in the other two directions. It is possible thus, in agreement with Mark and von Susich, to speak of a foil-like ordered micelle structure of stretched rubber. The evaluation of the diagram gave the following lattice constants:

$$a = 12.3 \pm 0.1 \text{ Å}$$
$$b = 8.3 \pm 0.1 \text{ Å}$$
$$c = 8.1 \pm 0.1 \text{ Å (fiber axis)}$$

Two different diagrams are obtained, according as the specimen is irradiated perpendicular to the plane of the thin film or parallel to it, with x-rays falling perpendicular to the direction of stretch. If during the exposure, the film is put in rotation, in such a manner that the direction of stretch lies in the axis of rotation, then the two diagrams are superposed with respect to the position of their spots, and there results a fiber diagram, such as has been described by various observers to date. In these diagrams, however, the serial order of the intensities of the individual interference spots varies with the conditions under which the picture is taken. The new method of placing the film in the direction of the pencil of x-rays, allows the accentuation of the interference spots dependent on the lattice spacing a or on the lattice spacing b, and thus allows the unique determination of a and b. If we now try to view the observed interferences according to their position and according to their intensities, in harmony with the rhombic symmetry of the ordered structure of the crystal system founded on micelles, there result for the three above-mentioned positions of the specimen (the two stationary, and one rotational), the schematic interference diagrams of Figures 88, 90 and 92. The actually observed diagrams corresponding to these are shown in Figures 89, 91 and 93. Figures 92 and 93 show the better known "common" fiber diagram. It is particularly worthy of note in these, that the sequence of intensities is different in the three diagrams, as can be seen. In Figures 88 and 89, the (200) plane has the greater intensity, in Figures 90 and 91, the (020) plane, and in Figures 92 and 93, the (020) plane. The axes calculated from this state of affairs, and the crystal system deduced from these axes, appear henceforth more certain than was the case with the older indications furnished by the work of Hauser and Mark. In these older measurements, the number of interference spots which were in agreement with the experimentally determined rhombic structure, both as regards their position and their intensity, were far too few to justify certainty in the conclusions. The lattice constant (Identitätsperiode) parallel to the fiber axis is incidentally newly determined by this work with somewhat greater accuracy, so that we are henceforth in a position to form quite definite conceptions of the size and orientation of the elementary lattice volume.[162]

The x-ray diagram shows that, in stretched rubber, an increasing fraction of the atoms or atom groups composing the substance become ordered in a lattice system, thus forming crystalline micelles (which do not have to be individually bounded by the same crystal planes), the size and the shape of

[162] Concerning the foundations of the lattice theory, *cf.* p. 151 of the text by J. Eggert mentioned above on p. 413; further, P. P. Ewald, "Kristalle und Röntgenstrahlen," Julius Springer, Berlin, 1929; also H. Mark, "Die Verwendung der Röntgenstrahlen in Chemie und Technik," J. A. Barth, Leipzig, 1926; and R. Glokker, "Materialprüfung mit Röntgenstrahlen," Julius Springer, Berlin, 1927.

which can be deduced from the width of the interference spots. The fundamental calculation of this nature (already presented by Hauser and Mark), supplemented by the new quantitative data, is repeated in the following form:

"Within an accuracy of about 100 per cent, it is possible to state that the length of the lattice element in the direction of the fibers and thus also the average length of the crystallites, is 300 to 600 Å, and the thickness and width of this lattice element, about 100 to 200 Å. Thus there is sufficient volume in each crystallite for about 10,000 to 20,000 unit cells, or 80,000 to 150,000 isoprene groups. From the fact that thin, greatly stretched films of rubber become oriented in a foil-like manner, as described above, it is reasonable to conclude that the micelle has the form of a long, flat box. From the intensity of the interference spots, it may be concluded that by all means the larger part, at least 80 per cent, of rubber in the stretched state is ordered in a lattice structure. From this we are justified in considering that part of the rubber which is capable of crystallization as the major part of rubber, and in using the x-ray in ascertaining its constitution."

Thus it follows from the axial length of the unit cell that it has a volume of $830 \pm 30 \times 10^{-24}$ cc., and (under certain assumptions regarding the true density of the crystalline part, which may be given the value 1) a mass of the same quantity in grams, corresponding to the mass of 8 isoprene groups. It may thus be concluded that 8 isoprene groups enter into the structure of one unit cell of rubber.[163]

In their studies on the chemistry of cellulose, Meyer and Mark developed the concept of the "principal valence chain." Staudinger[164] developed the concept of rubber as a "eucolloid," and emphasized the fact that this concept agrees with the physical behavior of rubber.[165] If these concepts are jointly applied to rubber, then we may imagine that there exist in the rubber micelle, principal valence chains of isoprene groups which unite in the form of helices whose axes are in the direction of the fiber axis. Indeed it must be assumed, if in agreement with Staudinger's conclusion, one rejects the idea of a "chemical" molecule consisting of perhaps only 2 or 4 isoprene groups, that these principal valences reach out beyond the unit cell and link together the entire box-shaped micelle. The constitution[166] of the principal valence chain, as proposed by Meyer and Mark, is as follows:

$$-CH_2-\underset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-$$

Consideration must be given to the further assumption that these chains stretch in the direction of elongation (*c*-axis), and that they unwind in the direction of the helical axis. From the length of the chain, (300-600 Å, indicating a series of 75 to 150 isoprene groups) the minimum size of the "structural molecule" can be determined. A comparison of these calculations with determinations by R. Pummerer is given on p. 489, to clarify the existing differences.

[163] It should not be forgotten, however, that when the numerical value of the density of stretched rubber is put into these calculations, values have been taken which deserve further experimental verification. Moreover, as with almost all previously determined quantitative constants of rubber, these values must also be redetermined, if in following the method of purification devised by Pummerer, well-defined rubber preparations become more accessible. It must further be remembered, as mentioned in the introduction to this treatise, that no pure preparations, but only technical specimens, have been available for x-ray diagrams to date.

[164] *Z. phys. Chem.*, **126**, 425 (1927); *Ber.*, **59**, 3019 (1926).

[165] Remark in discussion: *Z. Elektrochem.*, **31**, 468 (1925). See also the work of this author regarding the theory of the principal valence chain, in *Ber.* **61**, 2428 (1928), where reference is made to his ideas on this matter in the year 1920.

[166] No space will be given in this section to the question of the real chemical structure of rubber, which is treated exhaustively by R. Pummerer in another section of this text.

In Staudinger's [167] opinion, the real size of the chemical molecule of rubber is greater than the size calculated by Meyer and Mark, which is otherwise ll accepted. At the time of publication, the disagreement over this question as still active, so that a final opinion did not then appear possible, and only a reference to pertinent literature can be given. The investigation by Staudinger and his collaborators of other compounds of high molecular weight is of great importance (insofar as these [polyoxymethylene, etc.] can be considered as models of the rubber structure) because of the advantage of a well-known chemical structure.

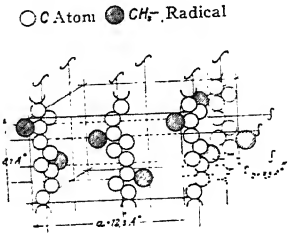


Figure 94

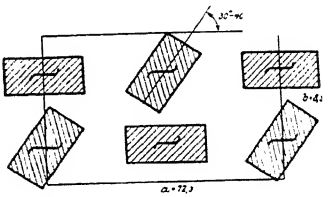


Figure 95

Three-dimensional and schematic representation of the unit cell of stretched rubber. (According to K. H. Meyer and H. Mark.)

The conclusions reached by Meyer and Mark are illustrated in Figures 94 and 95. The second, a schematic figure, shows clearly the hypothesis which is derived from these figures, that neighboring principal valence chains are oriented in the unit cell at various angles with the *a*-axis.

The co-existence of the transformation in rubber from the isotropic to the anisotropic form and of the reverse transformation, which had always been evident, was made visually apparent by the observation of the processes of extension and relaxation, as well as by observation of the x-ray screen. It must be assumed that the principal valence chains, which exist even in unstretched rubber, and which indicate the existence of a definite pre-formed structure, are transformed on relaxation into a condition of almost completely heterogeneous orientation, without entirely losing their micellar identity, however. This view is supported by qualitative considerations, and further substantiated by the phenomenon of the Gough-Joule effect which was required by the model of the alignment process, as first described by L. Hock.[168] In this model were described the pre-existence of lengthy chain-

[167] H. Staudinger, *Ber.*, **57**, 1206 (1924); see also the historical note, *Gummi-Ztg.*, **43**, 759 (1929). See also, the recent publications of Staudinger and collaborators: *Ber.*, **61**, 2427 (1928); **61**, 2575 (1928); **62**, 241 (1929); **62**, 263 (1929); **62**, 442 (1929); *Helv. Chim. Acta*, **11**, 1047 (1929); *Ann.*, **467**, 73 (1928); **468**, 1 (1929), *Z. angew. Chem.*, **42**, 37, 67 (1929); *Z. Krist.*, **70**, 193 (1929). There must also be mentioned the researches of J. R. Katz, made in an effort to determine the relation between x-ray structure and chemical constitution, e.g., those reported in *Z. phys. Chem.*, **125**, 321 (1927); *Kautschuk*, **3**, 215 *Gummi-Ztg.*, **41**, 2025, 2091 (1927); **1**, 53 (1 d rt *Kris* erence to metastyrene, *utschuk*, **3**, 106 (1927 Whitby, McNally and G— interested in other "elastic can be viewed in the same e.g., the polymers of vinyl acetate; *Trans. Roy. Soc. Can.*, **22**, 27 (1928). See also *India Rubber J.*, **75**, 3 (1928). In the section on swelling and solution of rubber, these subjects will again be considered. [168] *Kolloid-Z.*, **35**, 42 (1924).

like aggregates of molecules,[169] and their alignment into parallelism on extension of the rubber, as well as their simultaneous dense lateral packing, and the increase of the van der Waal (micellar) forces, which tended to fix the fiber structure.

The quantitative pursuit and more exact development of certain phases of these hypotheses have confirmed this basic concept in most essentials. The above-described thermal experiments, which show the van der Waal's forces to be in direct relationship to the observed thermal effects on extension, further corroborate the above concept.

Elasticity and Chemical Configuration. In the light of the success of the exact x-ray spectroscopy, there still remains the question regarding the interrelation of chemical constitution and elastic properties. The conviction has already been expressed in an article by L. Hock and P. Siedler [170] that a working hypothesis should include the following assumptions, namely: that the source of elasticity must be sought within the "macromolecule" (i.e., the micelle, or chain of molecules), and that the source of the elasticity of rubber must be found in the nature of its chemical constitution. In a more concrete manner, J. R. Katz [171] has expressed the thought that the rubber molecule may roll itself into a spiral form. With this concept, it is easy to understand the extensibility of the molecules. Concepts similar to these, but much more firmly based on structural analysis, were brought out by Meyer and Mark [172] with the conclusion that the principal valence chains of rubber "possess a definite tendency to bend and to coil up in a special manner." * Langmuir [173] also found occasion to assume the same kind of curvature of the extended molecules, as for those of certain fatty acids.

Further Theories of the Gough-Joule Effect. In returning to the Gough-Joule effect, it is necessary to study the attempts of other authors to explain the effects, although these disagree in part with the ideas which have already been given. These ideas must also be compared with the observed facts.

Swelling Theory of Hauser and Mark. Hauser and Mark [174] themselves based the following point of view on the fact that rubber is a two-phase system: the molecular aggregates in unstretched rubber (already frequently mentioned) exist in a swelled state, wherein the less associated phase is the swelling agent for the more actively associated phase, which latter may even become crystallized. In this state, the particles possess an extraordinarily large amplitude of heat motion, so that the intensity of the interference dots in x-ray observation is largely destroyed, exactly as would be the case under the influence of higher temperatures, and thus sharp interference patterns are practically impossible. Under unidirectional tension, during which alone the existence of interferences can be observed, a partial decrease of swelling of primary particles takes place, their internal order becomes more definite, and with this, the intensity of the interference pattern is increased. Their position is independent of the state of swelling. This concept does not, however, appear entirely acceptable, and has been rejected by both M. Ruhe-

[169] Compare also L. Hock, *Z. Elektrochem.*, **31**, 406 (1925) and also *Gummi-Ztg.*, **39**, 1741 (1925).

[170] *Kautschuk*, **1**, 10 (Oct. 1925).

[171] Unpublished article on the material presented at the principal meeting of the Kolloidgesellschaft, Nürnberg, (1925). Also, see J. R. Katz, "Ergebnisse exakt. Naturwiss.," Vol. 4, p. 175, Julius Springer, Berlin, **1925.**

[172] *Ber.*, **61**, 1944 (1928).

* Translator's Note. The molecular structure shown in Figures 94 and 95 has been further discussed by Hauser [*Ind. Eng. Chem.*, **21**, 249-51 (1929)], who assumed that rubber consists of long, helical, parallel chains which unwind during stretching.—N. J.

[173] *Cf.* p. 244 of Eggert's text; see also footnote 71, p. 413 of this text.

[174] *Kolloidchem. Beihefte*, **22**, 63 (1926).

mann and F. Simon.[175] This idea is also difficult to harmonize with the great rapidity of crystallization.[176] Obviously this concept is no longer represented in the work of Meyer and Mark.

An ingenious and careful study of the exact time required for the fiber structure to form in rubber has been made by W. E. Singer, J. D. Long, and W. P. Davey* [Paper read before the Chicago Meeting of the American Physical Society, June 24, 1933; see also *Ind. Eng. Chem.*, **24**, 54 (1932); *Rubber Chem. Tech.*, **5**, 30 (1932)]. Their determinations were made by means of a long series of very short x-ray exposures, taken intermittently during a repeated elongation and retraction cycle, but always at a definite time in that cycle. It was then possible to find the earliest time in the cycle at which "fibering" occurred. The authors state that "rubber must be of such a nature and such a structure as to account for the following characteristics: 1. A more or less critical temperature limit for the time lag of fibering. 2. A time lag of fibering unaffected by stretching the rubber above this critical temperature and then cooling rapidly. 3. A higher percentage stretch required to develop the fibrous structure after mechanical working and aging. 4. A relaxation time of less than 0.5 second. 5. A time lag of fibering independent of the length of time the rubber is held stretched, at least between 2 and 5 seconds. 6. A shorter time lag of fibering with a slow rate of stretching. 7. The enormous extensibility of rubber. All this mass of data is consistent with the picture that rubber consists of a tangle of spiral (or zigzag) shaped molecules whose ends are rather firmly anchored, but whose lengths can be temporarily untangled by the application of an external force."

Klein and Stamberger,[177] state that on extension, there is formed an ordered framework or network, whose elements are represented even in unstretched rubber. It is, however, necessary to add that depending on the spacing of this network (itself dependent on the extension), a variety of interference states would be expected. This is in contradiction to the observed facts.

X-Ray Diagram of Rubber. The x-ray diagram of rubber is independent of the source of the rubber. Worthy of note in this connection is the discovery of Hauser,[178] that experiments which were made on nearly 20 different kinds of rubber (different in respect to the country in which grown, the botanical family and genus of the plant, and thus of course, different in the form and size of the latex particles) have given x-ray diagrams which in respect to both their lattice spacing and their intensity distribution were in

[175] *Z. phys. Chem.*, **A138**, 1 (1928). *Cf.* p. 441 of this text.

[176] Meyer and Mark assume that in rubber subjected to 1000 per cent extension, there is at least 80 per cent "crystallized" substance, and it can be supposed that on greater extension the amount of this phase would still further increase. There will then not be much surplus of swelling agent when the rubber is again relaxed. Compare also the statement on p. 432 of this text concerning the refusal of very greatly stretched rubber to swell in benzene.

* Translator's note by N. J.

[177] *Kolloid-Z.*, **35**, 362 (1924). *Cf.* also p. 481 of this text. It must not be forgotten that the "forced crystallization" of rubber is a concept of an *obviously* specific nature, which can be likened to the "swarm concept" (Schwarmbildung) of crystalline liquids. A true crystallization from a state of complete chaos can not be proposed. The ever present micellar associations with their anisotropic principal valence chains represent a kind of chaotic cryptocrystallite (if one is permitted to suggest so contradictory a picture) which changes over into the well defined crystal modification on stretching. From this viewpoint, a kind of polymorphous transformation is not even to be considered, and the heat of extension corresponds to a heat of transformation. [Cf. *also* Hock, *Z. Elektrochem.*, **31**, 406 (1925).] On relaxation, the rubber succeeds in attaining a state of isotropy, which, however, because of the existence of a very marked stability of form, is not equivalent to the complete mutual independence in which the molecules exist in relation to each other in a true molten condition. (See p. 444.) The proportionately low values of the relaxation heats or "heats of fusion" of rubber (of the order of magnitude of 10 cal./gram) also appear to indicate that with its "melting" no interference occurs with the association of the molecules in any way comparable to that which occurs with other organic compounds.

Conversely, this molecular kinship of the rubber micelles, limited by the stability of form, becomes the more remarkable because the formation of the fiber structure must be carried out against the strongly opposing elastic forces of the form of the isotropic state. The stability of this structure would be impossible, as soon as "the potential energy of the stretched rubber was able to overcome the shear resistance of cohesive forces between the particles placed in parallel order." [L. Hock, *Kolloid-Z.*, **35**, 42 (1924)].

[178] *Naturwissenschaften*, **15**, 100 (1927).

complete agreement with the results already obtained for plantation rubber.[179] Since these kinds of rubber exhibit great differences in their physical and technological behavior, the only conclusion that can be drawn from these observations is that the existence of the interferences is largely independent of the mechanical properties of the rubber, and therefore is very closely connected with the inner structure of the molecular aggregate of the hydrocarbon itself. With this, the original thesis of Hock receives again a strong confirmation, in that this shows the seat of the phenomena connected with the anisotropy of rubber to be of molecular rather than of microscopic dimensions.

W. Ostwald's Theory of Accidental Formation of a Space Lattice. W. Ostwald considers the accidental formation of a space lattice as the source of the x-ray interference pattern. Ostwald, after the manner of O. Bütschlis and W. B. Hardy ascribes to the gelatinous contents of the latex cell a regular net-like structure, and assumes that in unstretched rubber the meshes of such a net are too large to give x-ray interferences. If, however, the latex particles are deformed into tubular bodies by the extension (*see* Fig. 96), then

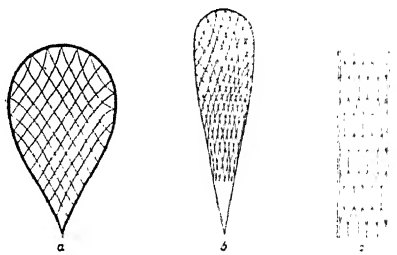


Figure 96—General character of the accidental crystal lattice formation.
(According to Wolfgang Ostwald.)

a. Original net-like structure of the latex particle;
b. and c. The partial and final deformations of this structure to an "X-ray density of packing."

the lattice spaces are thereby shrunk to such dimensions that they are capable of causing x-ray interferences. This theory originates also, as is well known, from the histological structure of the latex cells. Here again the conclusion is necessary, that the shape of the latex cell which has changed into a "crystalline body" must be dependent on the degree of extension existing for the time being, as this affects directly the dimensions of the micelle. This conclusion, however, is not consistent with the fixed position of the x-ray interferences. We are in need, then, of the additional assumption that with the beginning of "x-ray density of packing," a rigidity of the lattice elements also appears.[180]

On disturbance of the cellular structure, the effects mentioned must disappear. Nevertheless, Ostwald has considered it quite probable, that in a piece of rubber in which there has been complete breakdown of a cellular structure of the type he has described, such a structure would be regenerated

[179] It is, however, not stated with what degree of exactness this agreement was determined, so that small differences in the x-ray diagrams, such as those which could exist because of slight chemical impurity, are not denied.

[180] Insofar as with Ostwald, one accepts the debatable theory that the micelles are identical with the molecules or molecular aggregates, in just so far does one succeed in picturing the crystallites as of uniform size. If, however, this particular viewpoint is contrasted with that other special concept of the assemblage of the principal valence chains, as described by Meyer and Mark, then the quantitative relations produced by these authors are favorable to an obvious interpretation of the x-ray effect as crystal interferences. Besides, with Ostwald's theory, one misses the connection between the directional effect and both the change in density and the heat effect. The latter are left entirely out of consideration, inasmuch as the directional effect should not be conceived as a heat of compression, yet, as we have already proved, cannot be identified with the energy considerations of the stretch. (Compare p. 435 of this text.) We cannot do otherwise than require of the theory that the anisotropy, change in density, and heat effect must be considered in causal relationship.

by further deformation of the rubber. It is his opinion that even in an artificial rubber (which appears histologically free from all cell structure), deformation of the micellar network of the rubber could develop an "x-ray density" of the meshes of the network, which would give rise to at least a rudimentary x-ray pattern as observed in stretched natural rubber.[181]

X-Ray Survey of Vulcanizates and of Synthetic Rubbers. Finally it must be stated that in vulcanizates also, x-ray interference patterns have been observed, as was described in the first publications of J. R. Katz.[182]

These patterns are less marked than in raw rubber, but here also everything depends on the state of aggregation of the sample at hand. As long as there are reinforcing pigments or fillers in the compound, such as magnesium carbonate, whose particles themselves possess marked directional properties, one can determine to what extent they align their own long axis with the grain of the rubber (*see* p. 399).

Of importance also is the answer to the question of whether or not the anisotropy of stretched raw rubber remains the same in spite of vulcanization or chemical additions; i.e., whether there exists the possibility of topochemical reactions such as are observed in the case of cellulose. Related experiments carried out by H. Mark, G. von Susich and Hopff [183] have shown no results. The rubber derivatives produced (after addition of hydrogen, bromine, chlorine, iodine, halogen hydrides, and nitric oxide), after this treatment showed no x-ray pattern as did stretched raw rubber, but behaved like amorphous substances.[184]*

A very interesting recent observation of a well defined x-ray diffraction pattern for the synthetic material μ-polychloroprene, formed by spontaneous polymerization of chloroprene, has been made by W. H. Carothers, I. Williams, A. M. Collins, and J. E. Kirby† [*J. Am. Chem. Soc.*, **53**, 4203 (1931); *Rubber Chem. Tech.*, **5**, 7 (1932)]. They found the usual amorphous ring diagram for the unstretched polymer, indicating a spacing of 4.86 Å. At 500 per cent elongation, however, there appears a fully developed fiber diagram, indicating an identity period of 4.8 Å., which is identical with that found in β-gutta-percha.

Another chloroprene polymer, ω-polychloroprene, of a granular or globular nature, exhibits only an amorphous ring pattern. The x-ray patterns for an α-polymer, a β-polymer, and a balata-like polymer are not discussed.

Confirmation of the above determinations has been rendered by P. Garbsch and G. von Susich [*Kautschuk*, **8**, 122 (1932); *Rubber Chem. Tech.*, **6**, 113 (1933)] who found 4.8 ± 0.1 Å. for the identity period of the unstretched polymer, and at 600 per cent elongation, 4.81 ± 0.03 Å., comparing with 4.87 Å. for β-gutta-percha. These authors conclude that this polymeric product behaves just like amorphous natural rubber, in that its x-ray diagram departs from the amorphous pattern in the same way, and at about the same degree of elongation.

X-ray structural diagrams have been taken on a bromoprene polymer, showing a crystalline nature, but no quantitative data are presented [W. H. Carothers, J. E. Kirby, and A. M. Collins, *J. Am. Chem. Soc.*, **55**, 789 (1933); *Rubber Chem. Tech.*, **6**, 317 (1933)].

[181] The repeated production of the micellar structure could also be explained from the standpoint of the aggregation theory, just as are the "dead milling" ("Todwalzen") and the "recovery" of rubber. Compare also Meyer and Mark, *Ber.*, **61**, 1945 (1928).

[182] *Chem.-Ztg.*, **49**, 353 (1925), and also, Katz and Bing, *Z. angew. Chem.*, **38**, 439, 545 (1925), as well as J. R. Katz, "Ergebnisse exakt. Naturwiss.," Vol. 4, p. 154, Julius Springer, Berlin, **1925**.

[183] *Kolloid-Z.*, **46**, 19 (1928).

[184] After the manner of the concept developed on p. 433, the neighboring valences (fields of force) are removed, and thus there results a weakening of the micellar forces. This is brought about by virtue of the saturation of the double bonds of the rubber by the substances added. As a consequence of this action, the existence of the van der Waal forces between the directed aggregates is no longer possible. The anisotropic structure must therefore break down.

* Translator's Note. B. L. Johnson and Frank K. Cameron [*Ind. Eng. Chem.*, **25**, 1151 (1933)] have applied x-ray analysis to a study of the mechanism of rubber aging. They find

aspects of this work.)—N. J.

† Translator's note by N. J.

At the request of the author, Messrs. J. Eggert and Luft [185] have very obligingly repeated the same experiments with sulfur monochloride in the gaseous state, and also found negative results.[186]

Recently F. Kirchhof also published on the topochemical reactions of racked rubber,[187] wherein, after compounding with the halogens and halogen hydrides, the x-ray pattern was again caused to disappear, whereas on careful examination the fiber structure apparently remained unchanged. On the other hand, sulfocyclo-rubber gave a distinct pattern diagram, after intensification of the points. At the same time an increase of density was proved.

Of especial interest is the question of whether synthetic (or more correctly, artificial) rubber is also capable of producing x-ray interference patterns. Hock and Siedler [188] expected x-ray interference in synthetic rubber, because the anisotropy they had observed in this case appeared quite similar to that observed in natural rubber, although the property was not evident to the same degree.

Katz [189] obtained the first negative results with synthetic rubber which led to the conclusion that a positive, fundamental difference exists between natural and synthetic rubber. Although it is recognized that there are great differences between synthetic and natural rubber, both in their physical properties and in their chemical constitution (the latter clearly shown by experiments of Fromandi, recently carried out at the suggestion of the author), yet their common tendency to show a Gough-Joule effect betrays a rather obvious structural similarity. Hock [190] explained the failure to obtain interference patterns by the fact that the heat motion of the particles at room temperature, in the case of the synthetic rubber, so diminished the intensity of the interference spots—this had been earlier established on general theoretical grounds by Debye [191]—that no fiber diagram was obtained. He then planned to do the same work at lower temperature.

While these experiments were under way, in contradiction to his earlier publication, J. R. Katz [192] was able to show that he had obtained interference patterns in very greatly stretched synthetic rubber.

On the other hand, L. Hock and W. Barth [193] have succeeded in detecting interference patterns, in stretched synthetic rubber, which were definite but not very sharp. This work was performed in a chamber designed for low temperature work by F. Simon and Cl. von Simson.[194] The rubber was a methyl rubber W of glass-like transparency. The effect was first obtained only in the cold (— 60° C.), but remained at room temperature. The extensions to which the rubber was subjected were from 400 per cent to 1500 per cent.

It was necessary to make the extensions in the cold, as the anisotropy which should occur on extension at room temperatures was apparently lost by in-

[185] Scientific Laboratories of the "Agfa" Filmfabrik, Wolfen.

[186] Dr. R. Weil (Continental Caoutchouc- und Guttapercha-Compagnie, Hanover) some time ago was so obliging as to send the author a preparation which consisted of a thin sheet of rubber having a very strong calender grain (compare p. 424) and which had been placed in the curing bath directly after calendering. With this treatment, the sample had shrunk together to a shape that obviously showed the existence of a substantial fiber structure. However, an x-ray examination by Dr. Luft here again showed a negative result. Thus, even in spite of the obvious shrinkage, the inner isotropy had persisted.

[187] *Kautschuk*, **5**, 9 (1929).

[188] Hock and Siedler, *Kautschuk*, **2**, 88 (1926). L. Hock and G. Fromandi [*Kautschuk*, **5**, 81 (1929)] have expressly called attention to the significance of the chemico-structural dissimilarity between natural and artificial rubber from the standpoint of their colloid-chemical behavior. For later work and literature references, see pp. 433 and 491 of this book.

[189] J. R. Katz, *Kolloidchem. Beihefte*, Ambronn Festschrift, **23**, 344 (1926).

[190] *Kautschuk*, **3**, 126 (1929).

[191] *Ann. Phys.*, **43**, 49 (1914).

[192] *Chem.-Ztg.*, **51**, 53 (1927).

[193] *Z. physik. Chem.*, **134**, 271 (1928).

[194] *Naturwissenschaften*, **14**, 880 (1926); *Z. Physik*, **21**, 168 (1924); **25**, 160 (1924).

ternal slippage in the test piece. The careful studies of E. A. Hauser on the effects of rate of extension and temperature on the appearance and form of the anisotropy of natural rubber, had already been given careful consideration, even before these experiments. Thus, even during the stretching of the rubber test pieces in the chamber (in order to avoid the inner reversion to isotropy in spite of the externally maintained deformation), it became necessary to cool the strips with carbon dioxide snow. It was shown here also that synthetic rubber is far more similar to the liquid from which it was prepared than is natural rubber, as could have been concluded from the discussion of the Gough-Joule effect.

Voluntary Crystallization of Rubber, from the Viewpoint of Pummerer, Koch, and Gross. The voluntary crystallization of natural rubber, which has been discovered and described by Pummerer, Koch and Gross, is to be well differentiated from these "crystallizations" or fiber structures forced by unilateral tension, etc., which are entirely reversible.[195] In the preparation of pure rubber, they obtained some small, spheroidal crystals about 0.6 to 0.7 mm. in diameter, and proved the existence of a lattice structure, but obtained only a few interference spots compared with those obtained from stretched or frozen rubber. (*See* p. 447.) This is similar to one of the previously mentioned, irregular crystallizations of rubber which has been discussed on p. 168 of this book.[196]

The x-ray experiments on frozen rubber, which have been performed by J. R. Katz,[197] and E. A. Hauser and P. Rosbaud, show very decided Debye-Scherrer rings which indicate the existence of a mass of crystals of random orientation. These crystals and their orientation are voluntary. The observed positions of points in these interference patterns show again a remarkable agreement with those of the stretched rubber. (*See also* pp. 442 and 446.)

Various Physical Properties of Rubber

Preliminary Discussion

The special interest which attaches to rubber from the standpoint of physics or physical chemistry results from the unusual elastic and structural properties which it exhibits. Such other physical properties as it possesses in common with many other natural and artificial materials contribute only slightly to this special interest in rubber. The technological value of rubber is also based primarily upon its unique mechanical and elastic behavior, which permits it to be used in the electrical industry either where soft rubber is desired or where hard rubber is the preferred form. In electrical work, consequently, there are encountered compounds of various compositions, whose important physical properties are of more practical interest to engineers than of scientific interest to physicists. The figures previously presented in connection with electrical properties of rubber are therefore to be considered more as indications of the order of magnitude of the properties than of exact values for well-defined constants. There always remains the possibility of determining these constants with exactness in the case of pure rubber, however. The evaluation of the fundamental physical properties of the purest

[195] *Ann.*, **438**, 294 (1924). See also the contribution of Pummerer and Koch to this book, p. 168.

[196] Kondakoff remarked in this connection in *Caoutchouc & gutta-percha*, **22**, 12666-8 (1925) that he had obtained crystallized synthetic rubber in 1901. See also *Chem. Zentr.*, **96**, II, 692 (1925).

[197] "Ergebnisse exakt. Naturwiss.," Vol. 4, p. 161, Julius Springer, Berlin, **1925**.

possible rubber is to be considered as a very important problem. It seems that much work remains to be done along this line, although a beginning with respect to electrical data has been made by the United States Bureau of Standards. The study of the chemical constitution of rubber by German investigators has also provided opportunities for worth-while contributions to the store of information regarding physical constants of pure rubber. In this connection, careful determinations of heats of combustion, indices of refraction, spectral absorption of pure rubber (in solution), etc., have been made. (*See* p. 494.)

Calorimetric Data

Specific Heat. An exact knowledge of the behavior of the specific heat of raw rubber and of synthetic rubber of different kinds and different origins, may be obtained from the experiments of M. Ruhemann, and F. Simon, as well as from those of M. LeBlanc and M. Kröger, which have already been discussed in another connection. In their determinations, the latent heat effects coexist with transformation phenomena, and since these are dependent on the kind, state and previous history of the sample, no well-defined value for the specific heat of rubber can be given. It is of the order of magnitude of 0.4 cal./gram at room temperature. Even on different samples of the same kind of rubber, results are only fairly reproducible as shown earlier by Bostroem.[198] (*See also* pp. 436 and 441.)

Heat of Fusion. We have also had occasion to consider in another connection the "heat of fusion" of rubber, both in the stretched, frozen state, and in the normal frozen state. (*See* pp. 436 and 444, as well as p. 456, footnote 177.)

Heat of Combustion. The heat of combustion of rubber is 10,700 cal./gram. For comparison, the figure determined for gutta-percha is 10,740 cal./gram.[199] Heats of combustion were measured by F. Kirchhof and O. Matulka also. Clean, pale crepe gave 10,700 cal./gram. The rubber samples treated with sulfuric acid by these authors, gave somewhat lower values.*

Heat of Vulcanization. In a series of papers by J. T. Blake and by C. R. Boggs and J. T. Blake† [*Ind. Eng. Chem.*, **22**, 737-55 (1930)] the thermochemistry of vulcanization and various theories of vulcanization are discussed, and the work of others is reviewed. Weber [Weber, C. O., "Chemistry of India Rubber," pp. 106, 114, Griffin, London, **1912**] deduced by calculation that the heat of vulcanization was negative, and should amount to an absorption of about 450 cal. per gram of rubber at 3.8 per cent combined sulfur. Seidl [*Gummi-Ztg.*, **25**, 710, 748 (1911)] tried to explain the accelerating effect of litharge thermochemically. He considered the sulfur-litharge thermochemical reactions as being exothermic, but did not consider the heat of reaction of rubber and sulfur. Williams and Beaver [*Ind. Eng. Chem.*, **15**, 255 (1923)] found experimental evidence of the exothermic reaction of rubber, zinc oxide, sulfur and various accelerators. Rather inexact methods of calculation yielded values of heat of vulcanization of about

[198] *Kolloidchem. Beihefte*, **26**, 461 (1928).

[199] *Cf.* E. Geiger "Über die Konstitution der Hoch-Polymeren," Dissertation (**No. 422**), Technische Hochschule, Zürich, 31 (1926). Some rubber derivatives were also investigated. Polycyclic rubber, for example, gave only 10,584 cal./gram; polycyclic gutta-percha gave 10,596 cal./gram; hydrogenated rubber and hydrogenated gutta-percha gave 10,717 cal./gram and 10,741 cal./gram respectively. These values are very close to those determined for the pure substance itself. (These determinations are from the Eidgenössische Prüfungsanstalt für Brennstoffe, and were made by Dr. Schläpfer.)

* Translator's Note. Messenger [*Trans. Inst. Rubber Ind.*, **5**, 71 (1929)] has determined the heats of combustion of purified rubber, gutta-percha and balata in an attempt to determine if there were enough difference to throw light on the structural differences of these materials. He reports insufficient difference to allow any conclusions as to structure. His accuracy was not high, individual measurements of heat of combustion varying by as much as 4 per cent.—N. J.

† Translator's note by N. J.

10 cal. per gram of rubber at 10 per cent combined sulfur, in cases where total sulfur did not exceed 14 per cent. Kirchhof and Wagner [*Gummi-Ztg.*, **39**, 357, 372 (1925)] extended the work of Williams and Beaver to include other mineral pigments than zinc oxide. Kirchhof [*Gummi-Ztg.*, **39**, 892 (1925)] also studied the effect of various accelerators on heat evolution. The thermal effects were found to be enhanced, in litharge stocks, by the presence of natural resins. Perks [*J. Soc. Chem. Ind.*, **45**, 142T (1926)] using a slight modification of the method of Williams and Beaver, studied the heat of vulcanization of several rubber-sulfur mixtures from 0 to 32 per cent sulfur. He concluded from temperature-time curves that the reaction was slightly exothermic in the low combined sulfur range, and energetically exothermic in the ebonite, or high combined sulfur, range. Bostroem [*Kolloidchem. Beihefte*, **26**, 467 (1928)] has measured calorimetrically the heat of vulcanization of rubber with sulfur chloride in benzene solution, using a method developed by Hock [*Kautschuk*, **3**, 207 (1927)] for the measurement of heats of wetting. Bostroem found the heat of vulcanization to be exothermic to the extent of 5.9 cal. per gram of rubber.

J. T. Blake (loc. cit.) took advantage of the law of Hess, or the First Law of Thermodynamics, to simplify the experimental technique involved in measuring the heat of vulcanization. Since the initial and final states completely define the thermal interchange in the transition between these states, Blake determined heats of vulcanization simply by measuring heats of combustion of the raw and vulcanized compounds. To correct the heats measured to the heats at the vulcanization temperatures, specific heat calculations were made. Williams and Beaver (loc. cit.), who tried this method in a preliminary way, found no appreciable difference between the heats of combustion of a mixture of 6.5 per cent sulfur with 93.5 per cent rubber, vulcanized to 0.7 and 5.6 per cent combined sulfur respectively. They concluded that there was no appreciable heat of vulcanization for this combined sulfur range. The heats of combustion reported by Williams and Beaver appear to be seriously in error, as compared with accepted values, such as those of Kirchhof and Matulka [*Ber.*, **57B**, 1266 (1924)] and many others, as mentioned above. J. T. Blake reported as his own work by the heat of combustion method, that, for pure rubber-sulfur mixes, the heat of vulcanization was substantially zero up to 6 per cent combined sulfur, and then rose abruptly and nearly linearly to 442 cal. per gram of rubber at 32 per cent combined sulfur. With a pure gum stock of the following composition: smoked sheets 600, zinc oxide 30, sulfur 60, diphenylguanidine 4.5, the heat of vulcanization was found to be substantially zero up to 3.66 per cent combined sulfur, and to rise abruptly from this value to 65 cal. per gram of rubber at 8.5 per cent combined sulfur. No heat of vulcanization was found when *m*-dinitrobenzene or selenium were used in place of sulfur. This work was carried out with smoked sheets rather than with purified rubber. A good bibliography accompanies this publication of Blake's.

In a later research than that of Blake, K. Hada, K. Fukaya and T. Nakajima [*J. Rubber Soc. Japan*, **2**, 389-97 (1931); *Rubber Chem. Tech.*, **4**, 507-13 (1931)] obtained widely different results from those of Blake. They explain the difference by stating that besides heat of vulcanization, Blake had also included the heats of reaction of resins and proteins with sulfur, and the heat of combustion of some free sulfur. These authors used the heat of combustion method, but used purified materials and applied more precise corrections. Pure rubber was prepared by dissolution and precipitation, and the proteins were removed by trichloracetic acid. Vulcanization was carried out very completely. The vulcanized samples were extracted with, and kept in, acetone, which was distilled off *in vacuo* before combustion. The experimental results show the heat of vulcanization to be endothermic to the extent of 393 cal. per gram of sample at 0.75 per cent combined sulfur, and to change linearly through zero at a little more than 4 per cent combined sulfur, to a maximum exothermic value of nearly 700 cal. per gram of sample at about 11 per cent combined sulfur. With higher combined sulfur, the heat of vulcanization decreases linearly to a slightly endothermic value (40 cal. per gram of sample) at 23 per cent combined sulfur. This value apparently remains unchanged up to 30 per cent combined sulfur.

These investigators claim a good degree of accuracy in their determinations, except for two matters. First, the heat of combustion of their purified rubber was 10,495 cal. per gram, whereas the value found by Messenger (*see* p. 461, footnote), was 10,970 cal. per gram for very pure rubber. Second, they did not determine the heat of combustion of sulfur in their own apparatus, but used data as published. The internal temperature of the samples during vulcanization varied in a manner to be expected from the final results, an observation significantly different from that which should be expected on the basis of Blake's data.

In a study of the heat of reaction during vulcanization, Y. Toyabe [*J. Rubber Soc. Japan*, **2**, 251-4 (1930); *Rubber Chem. Tech.*, **4**, 514 (1931)] made several improvements in technique, and discovered some interesting relations between the thermochemical behavior during vulcanization and the type of accelerator used. But since no description is given of the type of rubber used, and no calculations are made of the heat of vulcanization, the discussion of the results of this work is confined to their bearing on accelerators.

Heat of Swelling. Hock undertook to measure the heat of swelling of rubber, in collaboration with Bostroem and Hartner,[200] who have already been mentioned in connection with determinations of the heat of stretching.[201] The heat of swelling of rubber is dependent on the nature of the swelling agent and even more so on the age and previous history of the sample. For this reason, it might be well to mention here that as a very sensitive test for the course of molecular aggregation as it progresses with time in solid rubber, the heat of swelling is also a good index, as are the changes in the mechanical properties. If one determines this heat of swelling on a freshly milled sample of pale crepe, frictioned on to a fine wire cloth for the sake of obtaining better thermal contact with the calorimetric liquid, one finds that in using benzene for a swelling agent, a value of about —0.1 cal./gram is obtained; that is, there is a cooling instead of a heating. If the same experiment is carried out on the same material 9 months later, after storage of the sample at room temperature, one finds a value of this quantity about 50 times as large. The difference may be spoken of as the heat of aggregation, and can be considered in relation to the ability to store elastic energy. This subject will be mentioned again in connection with the discussion of pigmentation. However, the swelled state of aged rubber is different from that of freshly milled rubber. This resulted, particularly in the work of F. Hartner, in the observation that on repeated swelling of aged rubber following intermediate drying, the same large value of the heat of swelling is found at each determination. However, renewed milling causes disaggregation and a small value of the heat of swelling is again observed.

By its very nature, the heat of swelling, so measured, is no simple phenomenon. This has been mentioned on p. 436. In the discussion of the swelling process itself, we will return to the complex character of these phenomena. (*See* p. 479.)

Heat Conductivity. Ira Williams [202] made an extensive survey of the thermal conductivity of rubber, not only in the form of crude plantation rubber, but also in the form of compounds. The thermal conductivity is that quantity of heat which passes in unit time through a cross section of rubber 1 cm. square when a thermal gradient of 1° C./cm. exists normal to this section. For smoked sheets Williams found the value 0.00032. He determined also the thermal conductivities of such pigments as zinc oxide, sulfur, carbon black, etc. (0.00082, 0.00166, 0.00067) and proved that for pigmented compounds the thermal conductivity was the sum of the conductivities of the component parts, considering these in their proper relative concentrations.[203]

Work on the thermal conductivity of vulcanized rubber compounds* is now (1934) being carried out in the laboratory of the translators by V. N. Morris. The method employed is a modification of one of those used by Ira Williams at the same laboratory in 1922. A thermocouple is inserted at the geometrical center of the sample of cured rubber, which

[200] *Cf.* the above-mentioned work of S. Bostroem and especially the dissertation of Fr. Hartner, Giessen, **1929**, and also L. Hock, *Z. Elektrochem.*, **34**, 662 (1928).

[201] *Cf.* also p. 435 of this text.

[202] *Ind. Eng. Chem.*, **15**, 154-7 (1923); *India Rubber J.*, **65**, 561 (1923).

[203] Numerical examples from Williams' work may be found, for example, in K. Gottlob, "Technologie der Kautschukwaren," p. 163, Braunschweig, Fr. Vieweg u. Sohn, **1925**.

* Translator's note by N. J.

is immersed in a bath of boiling water. From the original temperature of the sample, the surface temperature of the sample in the bath, and the temperature at the thermocouple, after a definite time of immersion in the bath, it is possible to calculate the diffusivity and hence the conductivity, the method of E. D. Williamson and L. H. Adams [*Phys. Rev.*, **14**, 99 (1919)] being used for the calculations.

C. E. Barnett* was kind enough to furnish the translators with a copy of his paper on "Thermal Properties of Rubber Compounds" previous to publication. [See *Ind. Eng. Chem.*, **26**, 303 (1934).] This investigator has used a flat plate conductivity method involving a central heater plate with guard ring and two rubber slabs conducting the heat to two outer metal plates at the lower temperature. Many well-planned precautions were taken, and the guard ring technique was developed to a high degree of accuracy. Some of the results were checked by an entirely different method, employing a spherical heater element imbedded in the center of a spherical sample. In all cases, many thermocouples were used to measure temperature uniformity over surfaces which the geometry of the experiment dictated should be isothermal. The chief emphasis was placed on variations of zinc oxides differing in particle size and curing rate. As stated by Williams, no difference was found between the thermal conductivities of cured and uncured rubber compounds. The results in Table 10a indicated that the figures obtained by Barnett agree in general with those of Williams. However, the figures for clay and magnesium carbonate are in reverse order to those of Williams, and those for antimony sulfide, sulfur and talc disagree somewhat.

TABLE 10a.—*Thermal Conductivity of Rubber Compounding Ingredients.*

Ingredient	Thermal Conductivity cal. cm./cm.² °C. sec. Williams	Barnett
Zinc Oxide, Fast Curing	.00166	.00167
Iron Oxide	.00132	.00132
Dixie Clay	.00058	.00106
Lithopone	.00094	.00092
Blanc Fixe	.00078	.00078
Zinc Sulfide	—	.00109
Whiting	.00084	.00084
Talc	.00058	.00090
Asbestine	—	.00098
Magnesium Carbonate	.00103	.00057
Antimony Sulfide	.00021[a]	.00027[b]
Carbon Black (Slow curing)	.00067	.00066
Carbon Black (Fast curing)	—	.00068
Lampblack	—	.00140
Graphite (Acheson)	—	.00217
Diphenylguanidine	—	.00034
Mercaptobenzothiazole	—	.00045
Sulfur	.00012	.000298
Rubber	.00032	.00032

[a] 12 per cent sulfur. [b] 0.9 per cent sulfur.

A. A. Somerville [204] ascertained the relative thermal conductivities of a few rubber compounds by a very simple method, by using a stack of slabs laid together with thermocouples placed between them. Their area was 7 by 7 inches, and they were 0.1 inch in thickness. The lower face of the stack was warmed by boiling water and the other was cooled with ice. After 3 or 4 hours, a steady state of thermal flow was reached, and the relative thermal conductivities could be very simply calculated from the temperatures between the slabs. The state of cure was without apparent influence on the thermal conductivity, but various pigments caused changes in the values. Likewise, in an investigation of many substances of low conductivity, Ezer Griffiths and G. W. C. Kaye [205] using this same technique with slabs of the various materials, measured the conductivity of rubber and rubber compounds.

* Translator's note by N. J.

[204] *India Rubber J.*, **62**, 94 (1921); *Rubber Age (N. Y.)*, **9**, 131 (1921).

[205] *Proc. Roy. Soc. (London)*, **A104**, 71-98 (1923). See also *Chem. Zentr.*, **95**, I, 2802 (1924). Here reference is given to an experiment of F. A. Giacomini which proved the P. Debye theory of thermal conductivity in crystals. The same investigator made measurements in ebonite, *Ber. deut. physik. Ges.*, **20**, 94-96 (1918).

The thermal conductivity of stretched rubber has not yet been determined, but interesting information would be expected from such work because of the anisotropy of the substance. The author would like to reserve for himself the performance of these experiments for which preparations have already been made.

Optical Data

Indices of refraction have been determined by G. S. Whitby[206] and also by Staudinger and his collaborators. The value $n_D = 1.5222$ was obtained by Geiger.[207] For a density $d_4^{16} = 0.920$, the molecular refraction, calculated on the basis of the isoprene molecule, becomes

$$\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = 22.57$$

With the assumption of a double structure of the isoprene group, this agrees excellently with the theoretical value of $M_D = 22.62$.

D. F. Twiss[208] extended his work in this same field to gutta-percha, and found with $n_D^{15} = 1.525$, a value of M_D almost the same for gutta-percha as for rubber.†

Optical properties of the recently developed synthetic material chloroprene and its polymers have been measured by W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby* [*J. Am. Chem. Soc.*, **53**, 4203 (1931); *Rubber Chem. Tech.*, **5**, 7 (1932)]. They find for chloroprene, $d_{20}^{20} = .9583$ and $n_D^{20} = 1.4583$ and $M_D = 25.26$ which agree well with calculated values for a formula C_4H_5Cl.

For the spontaneous polymerization product μ-polychloroprene, they find $d_{20}^{20} = 1.23$ and $n_D^{20} = 1.5512$. For the α-polymer, very similar figures are obtained. Both these polymers are useful as synthetic rubber, whereas other polymers, such as the β- and ω-forms and a balata-like form, have not been found so useful.

Further optical data on synthetic rubber-like products similar to the above-mentioned chloroprene products are given by W. H. Carothers and D. D. Coffman [*J. Am. Chem. Soc.*, **54**, 4071 (1932); *Rubber Chem. Tech.*, **6**, 115 (1933)] and by W. H. Carothers, G. J. Berchet, and A. M. Collins [*J. Am. Chem. Soc.*, **54**, 4066 (1932); *Rubber Chem. Tech.*, **6**, 121 (1933)].

The optical properties of an ether-soluble rubber hydrocarbon have been measured by C. P. Saylor [W. H. Smith, C. P. Saylor, and H. J. Wing, *Bur. Standards J. Research*, **10**, 479 (1933); Bur. Standards Research Paper No. 544; *Rubber Chem. Tech.*, **6**, 351 (1933)]. His crystalline spherulites were about 0.05 mm. in diameter, and the individual needles composing these spherulites were about 20 microns by 1 or 2 microns in size. By the method of immersion in an aqueous solution of potassium mercuric iodide, the refractive indices ϵ and ω were determined at $-5°$ C. The crystals were found to have negative elongation, as indicated by these indices:

$$\epsilon = 1.535 \pm 0.003$$
$$\omega = 1.583 \pm 0.003$$

In the melted state, at 11° C., the refractive index was found to be 1.525, which agrees

[206] *Trans. Roy. Soc. Can.*, **18**, III, 191 (1924). Concerning the concept and the theoretical calculation of the molecular refraction, which is here calculated on the molecular weight of isoprene, since the molecular weight of rubber is unknown, see p. 489 of this text, and p. 148 of the textbook by J. Eggert. The molecular refraction experimentally observed agrees very satisfactorily with that calculated on the assumption of a double bond in each isoprene group. (See also the following footnote.)

[207] *Cf.* the above-mentioned Dissertation, p. 27. Further, see Kirchhof and Matulka, *Ber.*, **57**, 1266 (1924); these authors found the density, d_4^{20} to be 0.920. Macallam and Whitby obtained the following data: $d_4^{20} = 0.9237$, $n_D = 1.5219$, and from these figures, $M_D = 22.46$. In the cases of hydrogenated plantation rubber and hydrogenated gutta-percha, Geiger determined that the density and the refractive index (*loc. cit.*, p. 50) were smaller, and the molecular refraction was thus increased to 32.90 and 32.89 respectively. (The theoretical value is 32.95.)

[208] *Nature*, **113**, 822 (1924).

† Translator's Note. A sample of synthetic isoprene carefully prepared by H. J. Waterman and H. A. van Westen [*Rec. trav. chim.*, **48**, 1084-6 (1929); *Chem. Abstracts*, **24**, 824 (1930)] shows the following optical properties: $n_D^{20} = 1.4194$ and molecular refraction $M_D = 25.29$.—N. J.

* Translator's note by N. J.

well with McPherson's [A. T. McPherson, *Bur. Standards J. Research*, **8**, 757 (1932)] value of 1.5236 at 11° C., for the whole rubber hydrocarbon. The melting point of these needle spherulites is consistently between 9.5° C. and 11° C.

The optical properties of some of the fractions of destructive distillation of sodium rubber have been measured by T. Midgley, Jr., A. L. Henne, and A. F. Shepard [*J. Am. Chem. Soc.*, **54**, 381 (1932); *Rubber Chem. Tech.*, **5**, 1 (1932)]. Both saturated and unsaturated distillation products were examined. The refractive indices varied from $n_D^{25} = 1.4023$ to 1.4709.

The double refraction which occurs in rubber on stretching, has already been considered in connection with the Gough-Joule effect. With this double refraction, there occurs simultaneously a change in the dielectric strength in the principal directions of stress.

Along with the older work of Bjerkén on this matter, reference must be made especially to a series of further investigations of P. Rossi,[209] which, however, are essentially limited to the proof of a single discovery. Detailed descriptions of experiments to give an insight into the distribution of the tension within the elastically deformed rubber are described by O. Lehmann,[210] in which both tension and compression are used.[211] More recently, similar investigations have been taken up again, occasioned by the study of lamellar packing of rubber (*see* p. 399). This work has been done by M. Kröger.[212] The original articles give a wealth of information about the phenomena observed in the various experimental conditions. The results of Kröger's work can be summarized as follows: The lengthwise stretching produces a biaxial, positive, and lamellar deformation, and a weak, biaxial, negative double refraction. On storage of the rubber, also, a double refraction appears.

Inasmuch as the appearance of double refraction is a general result of mechanical stress, and is not specifically related to rubber, those investigations which attempt to measure the quantitative relation between the degree of double refraction and the degree of stretch, and also its relation to the Gough-Joule effect, deserve special interest. A beginning is made in this direction in a very recent investigation by W. C. van Geel and I. G. Eymers.[213] For small extensions up to a stretch of about 70 per cent at which the first interference patterns become noticeable, and the heat of stretching begins to be measurable, these authors found a functional relationship between the amount of the double refraction and the prevailing elongation. Beyond this boundary there begins a region in which the double refraction is proportional to the tension. Unfortunately, however, this relation does not hold in the region of higher tensions, in which characteristic changes occur in the structure of the rubber. However, investigation in this region has been initiated in the meantime, at the suggestion of H. Zocher.[214] The results of this work may be said to be in agreement with the previously discussed concepts of the structure of stretched rubber.*

Absorption of Light. Exact determinations of the absorption of light

[209] *N. Cimento*, (5), **20**, 226, 268 (1910). *Rend. di Napoli*, (3), **16**, 125, 142 (1910). *N. Cimento*, (6), **2**, 151 (1911). *Beibl. Ann. Physik*, **35**, 206, 364 (1911) and **36**, 67 (1912) as well as *Fortschr. Physik*, **2**, 394 (1910).

[210] "Molecularphysik," Vol. 1, p. 51, Wilhelm Englemann, Leipzig, **1888**.

[211] In this connection, reference should be made to methods and problems of photoelasticity, on which M. Wächtler has published a summary in *Phys. Z.*, **29**, 497 (1928): "Über die Anwendung der Akzidentellen Doppelbrechung zum Studium der Spannungsverteilung in beanspruchten Körpern."

[212] *Kolloid-Z.*, **45**, 46-52; 52-56 (1928).

[213] Note added in proof reading. The authors had the kindness to advise me of the contents of this article before its publication in the *Z. physik. Chem.*, **B 3**, 240 (1929), so that a brief reference could be made here to their work.

[214] Address at the convention of the Deutsche Kautschukgesellschaft at Hanover (May, 1929). H. Zocher and H. J. von Fischer, *Kautschuk*, **5**, 173 (1929); *Chem. Abstracts*, **23**, 5061 (1929).

* Translator's Note. H. Zocher and H. J. von Fischer [*Kautschuk*, **5**, 173 (1929); *Chem. Abstracts*, **23**, 5061 (1929)] measured the double refraction of rubber under a condition of uniform, bilaterally symmetrical stretching

by specific rubber preparations have been made only in solutions; consequently this matter will be given further consideration when rubber solutions are discussed (G. Scheibe and R. Pummerer). (*See* p. 494.) M. Kröger and H. Staude[215] have measured the light absorption of stretched and normal rubber in thin films. They determined the ultra-violet limit of absorption of rubber, and found the same result in a qualitative sense, and the same estimated degree of absorption as in measurements on solutions. They also showed that optical lenses could be made from thin, transparent rubber membranes swelled into the form of spherical segments by means of liquids, and stated that for certain applications in the ultra-violet, they are suitable to replace large quartz lenses. The thickness of the membranes examined for this purpose ranged from 0.1 to 1 mm. In the case of artificial rubber, these authors found the initial absorption at 2500 Å, and for pale crepe at 3000 Å, but when in the form of a stretched membrane, at 2300 Å.

Region of Long Wave Lengths. A few references will facilitate the access of the readers to the literature concerning the close relationship between the index of refraction, the reflection coefficient, and the dielectric constant, especially in the region of long wave lengths.[216] In these references are to be found determinations of these data on numerous materials, including various kinds of vulcanized rubber.

Effect of Light. The effects of light on rubber may be classified as chemical and physical. If air is excluded, and the radiation is of short wave lengths such as occur in sunlight, and especially in strong sources of ultra-violet light, the inception of disintegration and polymerization in thin films of raw rubber can be determined. These phenomena become evident in the films irradiated with light of 2,000 to 3,000 Å wave length by the increasing insolubility of the irradiated rubber. Extensive investigations of these phenomena have been made by Keiichiro Asano[217] after B. D. Porritt[218] had earlier observed that before the access of air, protected rubber solutions gave rise to the formation of gels under the influence of ultra-violet light. Finally, there is an interesting discovery of F. Kirchhof,[219] who found that

at a constant rate. A Berek calcite compensator was used. The effects of rate of stretching, mastication, degree of vulcanization and temperature were studied and the results were correlated with the mechanical properties. The conclusion of Zocher and von Fischer was that, instead of the x-ray interferences arising from crystals already present as a coherent mass (Hauser & Mark), the impurities present form the coherent mass, from which the crystallizable substance is expelled by the stretching (which causes simultaneous lateral compression). The pure material thus separated has the opportunity to crystallize into a discontinuous phase. This hypothesis allows a simple explanation of the differences in the "melting point," and also allows the Joule-Thomson heat effect to be considered simply as a heat of crystallization.—N. J.

[215] *Gummi-Ztg.*, **43**, 22-24 (1928). See also *Chem. Zentr.*, **99**, II, 2293 (1928). Concerning the absorptive capacity for x-rays of ordinary rubber, and of preparations containing lead compounds, work was carried out by G. W. Kaye, and E. A. Owen, *Chem. News*, **127**, 122-125 (1923). They determined also the electrical breakdown resistance of rubber stocks compounded with litharge to be from 5,000 to 12,000 volts per mm. (See the following section.)

[216] In this connection the first work to be mentioned is that of H. Rubens [e.g., *Ber. Preuss. Akad. Wiss.*, **38**, 556 (1917)] concerning the refractive indices of a few materials for short Hertzian waves ($\nu = 5.2 \times 10^9$). For instance, ebonite gives a refractive index of 1.64 for this wave length. See also, *Ibid.*, pp. 1280-1293 (1916), dealing with the reflection coefficient and the dielectric constant of some amorphous materials, e.g., of ground and polished hard rubber. In the spectral region between $\lambda = 10$ m. and $\lambda = 0.3$ mm., the refractive index remains practically constant, and no dispersion exists. See also R. Jaeger, *Ann. Physik*, (4), **53**, 409-460 (1917) for dielectric constants of solid bodies at various wave lengths. See also the following section of this text, in which there are further references on the dielectric constant.

[217] *India Rubber J.*, **70**, 307, 347, 389 (1925).

[218] *India Rubber J.*, **60**, 1159-1162 (1920). The same study was also made by V. Henri (*Caoutchouc & gutta-percha*, **7**, 4371 (1910), who learned that in its sensitivity to light, raw rubber is considerably superior to vulcanized rubber. This is explained by the assumption of Asano that the polymerization by light is similar to the effect of vulcanization. In most cases, Porritt connects chemical processes with the effects of light.

[219] *Kautschuk*, **3**, 28-30 (1927). Mention should here be made of an article by L. Raybaud [*Compt. rend.*, **149**, 985 (1910); also *Compt. rend. soc. biol.*, **71**, 216-8 (1910)] concerning the deleterious effect of sunlight on rubber.

the formation of a gel is observed when a benzene solution of rubber is subjected to ultra-violet radiation in the presence of yellow phosphorus. Zinc xanthate accelerates this reaction. Diffuse daylight apparently has no effect.*

Electrical Properties

The electrical properties of rubber are of great technological importance. For the most part these have been determined for the technically important types of compounds, using common commercial rubber. So far, the known data are not of the nature of characteristic constants of matter. Since the United States Bureau of Standards appears to be engaged in determining the electrical properties of well-defined raw materials including pure rubber, this deficiency in the data may well be filled in a reasonable length of time.† It is apparent from the communications submitted, that purified rubber, of supposedly the same degree of aggregation as raw rubber, both by itself and in compounds, shows electrical properties obviously different from those of a technical grade of raw material.[220]

The work of Scott, McPherson and Curtis‡ referred to above covers compounds from 0 to 32 per cent sulfur, temperatures from −75° C. to 235° C., and frequencies from 60 to 300,000 cycles per second. Complex properties are found for these rubber sulfur compounds. There is a "ridge" of high properties (dielectric constant, power factor or conductivity) on the temperature—per cent sulfur graphs running from low temperature-low sulfur content to high temperature-high sulfur content. The highest values of the properties are found in the neighborhood of 20 per cent sulfur and 75° C. in the case of power factor and conductivity; in the case of dielectric constant, the maximum values appear to be above the limits of experiment, both in temperature and per cent sulfur. On both sides of these plotted "ridges" of high properties, large regions on the plot indicate low properties. The decrease in dielectric constant in the case of higher sulfur content or lower temperature is more rapid than in the direction of higher temperature or lower sulfurs. In the cases of power factor and conductivity, the ridge is steeper and more symmetrical. There is a region above 175° C. in which much higher power factor figures again appear, at lower frequencies. This similar behavior of power factor and electrical conductivity is to be expected. A brief résumé is given to compare the properties of purified and crude rubber compounds, and to discuss the selection of rubber compounds for specific uses.

In evaluating these physical properties, only their order of magnitude can be conclusively stated, rather than definite numerical values. For this reason, a comparison will be made of those electrical properties of natural and artificial rubber which show remarkable agreement.

The United States Bureau of Standards,[221] in an extensive investigation, has determined those electrical properties which are most important from a technical standpoint, especially in comparison with the corresponding behavior of gutta-percha.

* Translator's Note. Emil Ott [*J. Am. Chem. Soc.*, **52**, 4612 (1930); *Rubber Chem. Tech.*, **4**, 82 (1931)] described briefly the interesting fact that on exposure of translucent crepe rubber to x-rays, the irradiated spot became more opaque, and the interference pattern sharper, indicating an increase in crystalline particle size, and a progressive crystallization. The region thus affected was sharply defined by the edges of the beam, and disappeared easily on warming of the sample. This sample of rubber is the same one as described in a previous article [*Naturwissenschaften*, **14**, 320 (1926).] In the case of gutta-percha, a similar activation of crystallization in ultra-violet light was noted by Kirchhof [*Kautschuk*, **4**, 254 (1929); *Chem. Abstracts*, **23**, 1525 (1929)].—N. J.

† Translator's Note. The work on pure rubber undoubtedly referred to is that of A. H. Scott, A. T. McPherson and H. L. Curtis, which has recently been published in the *Bureau of Standards Journal of Research*, **11**, 173-206 (1933), and reprinted as *Research Paper No. R. P. 585*, "The Effect of Temperature and Frequency on the Dielectric Constant, Power Factor and Conductivity of Compounds of Purified Rubber and Sulfur."—N. J.

[220] Notes from the U. S. Bureau of Standards, communicated by the Director; *J. Franklin Inst.*, **205**, 125 (1928).

‡ Translator's note by N. J.

[221] See H. L. Curtis and A. T. McPherson, *Bur. Standards Tech. Paper*, **No. 299**. See also the article in the *India Rubber J.*, **71**, 235 (1926), as well as in *Kautschuk*, **2**, 67 (1926).

Supplementing the older work of Schiller, mentioned on p. 418 in connection with the discussion of the anisotropy of stretched rubber, the dielectric constant has been determined for numerous rubber samples. This constant will hereafter be designated ϵ. Pale crepe gave the value $\epsilon = 2.43$; smoked sheets gave $\epsilon = 2.53$, and after one year's natural aging, $\epsilon = 2.38$. In pure rubber-sulfur compounds, ϵ increases in proportion to the amount of sulfur present, as well as with the curing time, except that in the case of hard rubber containing 30 per cent sulfur, it is not noticeably greater than in compounds of 8 per cent sulfur content. The values of ϵ vary for these vulcanized samples from 2.4 to 3.5. The theoretical requirement that ϵ shall be equal to the square of the refractive index is hereby quite well satisfied.[222]

D. W. Kitchin* [*Ind. Eng. Chem.*, **24**, 549 (1932); *Rubber Chem. Tech.*, **5**, 367 (1932)] in the fifth of a series of "Studies in the Vulcanization of Rubber," discusses the effect of per cent sulphur, temperature and electrical frequency on the dielectric constant and power factor of vulcanized rubber. "Data are given for samples containing from 2 to 32% sulphur tested at 30°, 50°, 75° and 100° C. at frequencies from 600 to 2,000,000 cycles. These electrical properties vary greatly with composition, frequency and temperature. The dielectric behavior has been interpreted in previous papers [C. R. Boggs & J. T. Blake, *Ind. Eng. Chem.*, **22**, 748 (1930); D. W. Kitchin, *Trans. Am. Inst. Elec. Engrs.*, **48**, 495 (1929)] on the basis of polar molecules. In this paper it is shown that this theory, as originally applied to rubber, requires some modification. The results do not disprove the dipole mechanism, but they do show that the low dielectric constant and power factor of hard rubber at room temperature, which led to the belief that addition of sulphur to all the double bonds gave a balanced molecule, are really due to its rigidity which so retards the electrical response that the period of charge or discharge is 24 hours or more. At higher temperature hard rubber softens, the period becomes short, and dielectric constant and power factor are high.

Studies of the compressibility and thermal expansion of vulcanized rubber have revealed two states with a fairly sharp transition temperature: a hard state in which rubber resembles a solid, and a soft state in which it exhibits properties of a viscous liquid. The dielectric behavior is also greatly influenced by this transition and in a manner which gives additional support to the concept of soft rubber as a liquid.

It is shown that the agents producing the electrical effect are not identical, but possess widely different relaxation times. Preliminary tests show that the power factor of a vulcanized rubber sheet decreases on stretch. None of the data makes it possible to determine the actual mechanism of the electrical behavior."

The nature of the pigments is of considerable influence on the dielectric constant of compounds in general, as they cause a great increase in the value of this constant. Thus, in case 20 per cent of gas black is milled into rubber, its dielectric constant increases to $\epsilon = 6$. The effect of moisture content also plays an important role. A comparison with gutta-percha shows that in the pure state, these materials exhibit substantially the same value, an observation which was to be expected from the similarity of their chemical constitution.

The electrical resistance of raw rubber is of the order of magnitude of 10^{14} ohms per cm. cube, the actual figures being, for pale crepe, 50×10^{14}, for Para rubber, 35×10^{14}, for smoked sheets, 3×10^{14}. Pure gutta-percha exceeds rubber in this respect by a considerable amount (370×10^{14}). The common gutta-percha of commerce, containing resin and dirt and (in the

[222] See also the quotation concerning dielectric constants in the previous section. Also in the older literature, see N. Schiller, *Pogg. Ann.*, **152**, 535 (1874), and J. E. H. Gordon, *Phil. Trans. Roy. Soc. (London)*, **170**, I, 417 (1879). These authors determined for raw rubber, $\epsilon = 2.12$ (Schiller) and 2.22 (Gordon); and 2.60 (Schiller) and 2.49 (Gordon), extrapolated to infinite wave length. These measurements should be considered along with newer measurements of Liebisch and Rubens [*Ber. Preuss. Akad. Wiss.*, p. 876 (1919) and p. 211 (1921)], who found for $\lambda = 3 \times 10^{-2}$ cm., $\epsilon = 2.61$ for natural rubber, and $\epsilon = 2.56$ for synthetic rubber.

* Translator's note by N. J.

sample examined) only about 57 per cent gutta-percha, still exhibited a resistance of 25×10^{14} ohms per cm. cube.

Pure rubber-sulfur vulcanizates show no particular difference from raw rubber with respect to their electrical resistance. Pigments, however, have a great effect on this property. Litharge increases the resistance, but gas black reduces it enormously, 25 per cent of black reducing the value to 10^{13}, 35 per cent of black, to 10^{8}, or a reduction to 10^{-5} of the value for the unpigmented rubber. With regard to dielectric loss,[223] raw rubber and pure gutta-percha are similar, though with increased content of resin, the loss increases in gutta-percha. Pigments increase the dielectric loss decidedly. In a compound containing 20 per cent gas black, the loss is 80 times greater than that of the unpigmented rubber, and in a compound containing 50 per cent litharge, it is 20 times as great. As the final result of this whole investigation, it was determined that rubber lends itself better to the construction of cables than gutta-percha, in that it shows more favorable dielectric properties.

McPherson, Curtis, and Scott[224] have studied the interrelation of density and electrical properties in the system rubber-sulfur. With increasing sulfur content, the density increases directly with the composition, up to a 19 per cent sulfur content, where an instability occurs. The ϵ increases with sulfur content up to a concentration of 10.5 per cent, decreases in vulcanizates containing 10.5 per cent to 19 per cent of sulfur, and then gradually rises again. The power factor follows a similar course, with a maximum at 13.5 per cent. The electrical resistance increases until a concentration of 26 per cent is reached, and then decreases. The authors show the relation between the point of instability and the stoichiometric relation of the definite compound $(C_5H_8)_2S$ which contains 19 per cent sulfur.*

There are numerous other articles on important electrical properties of rubber, which cannot even be discussed here. The mention of some of these papers will have to suffice.[225]†

[223] See, e.g., F. Kohlrausch, "Handbuch der Praktischen Physik."

[224] *Bur. Standards Sci. Paper*, **No. 560**, 36 pp. (1927).

* Translator's Note. The effects of different accelerators and antioxidants in rubber compounds on the alternating current conductance, specific resistivity, power factor, dielectric constant and water absorption are discussed by J. H. Ingmanson, C. W. Scharp, and R. L. Taylor [*Ind. Eng. Chem.*, **25**, 83-87 (1933)]. They find that in high grade soft rubber insulation compounds, the highest resistivity was obtained with a thiuram accelerator. In the case of compounds containing 1.35 per cent sulfur, the power factor was found to increase with increasing time of cure. The choice of antioxidant was found to have some effect on the electrical properties, but not of such a nature as to "be attributed directly to differences in chemical structure of the antioxidants."—N. J.

[225] With reference to the work last discussed above, W. H. Nuttall [*Trans. Inst. Rubber Ind.*, **4**, 313 (1928)] has studied the electrical insulating materials, especially from the chemical point of view. He comes to the conclusion that well polymerized materials are best qualified to be insulators, and that special attention must be paid to the use of the purest possible materials. St. Reiner reported on rubber as a dielectric [*Gummi-Ztg.*, **41**, 929 (1927)] and on gutta-percha in the same capacity [*Kautschuk*, **4**, 55-56 (1928)]. P. Dunsheath [*Trans. Inst. Rubber Ind.*, **2**, 460-87 (1927)] also investigated the electric properties of rubber as affected by pigmentation, moisture, curing time, etc. An investigation by Hikoo Saegusa [*Science Repts. Tohôku Imp. Univ.*, **13**, 179-185 (1924)] and also *Chem. Zentr.*, **96, I**, 2616 (1925)] deals with dielectric hysteresis, etc., of rubber as well as of ebonite. The same author published later [*Ibid.*, **14**, 335 (1925) and *Chem. Zentr.*, **97, I**, 316 (1926)] on the change of the ratio of conductivity to capacity with the temperature. Chr. Roos [*Z. Physik*, **36**, 18 (1926)] tried to increase the conductivity of ebonite and the other solid dielectric materials by irradiation with x-rays.

G. E. Bairsto determined the dependence of the dielectric constant on the frequency for both gutta-percha and rubber, in the frequency range commonly used in wireless telegraphy. He found a gradual decrease in its numerical value with increasing frequency. [*Proc. Roy. Soc. (London)*, **A 96**, 363-382 (1920)].

J. Villey, P. Vernotte and H. Lacaze investigated the relation between the ohmic resistance of rubber and its dielectric polarization. The conductivity of a slab of rubber 3 mm. thick was measured, and a hyperbolic decrease of current with time was found. This experiment showed the current attenuation to be very sensitive to temperature. [*Compt. rend.*, **178**, 1612 (1924)]. Finally, an investigation by Donald W. Kitchin is described [*India Rubber J.*, **77**, 327 (1929)] which dealt with the power factor and dielectric constant in viscous dielectrics.

† Translator's Note. A later review of electrical researches is furnished by W. H. Nuttall and J. Kirkwood [*India Rubber J.*, **80**, 657 (1930)].—N. J.

A comparison of the electrical properties of natural rubber and synthetic rubber (methyl rubber of types H and W) has been made by K. Geisler.[226] He was able to prove that compounds of synthetic rubber were completely similar to those of natural rubber, insofar as their insulation resistance was concerned, and also that the dielectric losses of the two kinds of rubber were of the same order of magnitude. Cable compounds show almost exactly similar properties, whether made from artificial or natural rubber. Occasionally, the properties of the artificial rubber are slightly superior to those of the natural rubber. The similarity between artificial rubber and natural rubber is much greater in their electrical properties than in their mechanical properties.

This fact is not difficult to understand, inasmuch as the electrical properties are dependent on the chemical nature of the rubber molecule, whereas the mechanical properties are dependent on the physical state of the structure (aggregation, etc.). In chemical constitution, artificial and natural rubber are not dissimilar, as they are in their degree of aggregation. In particular, hard rubber slabs made from artificial rubber present just as good insulating properties as those made from natural rubber, in that they will withstand 70,000 to 80,000 volts per mm. of thickness.[227]

In connection with the investigations just discussed concerning the electrotechnical considerations, there are a few other observations that should be mentioned. L. Bouchet [228] was able to prove that under the influence of an electrostatic field, vulcanized rubber contracted in the direction of the field. He also determined the change in thickness of a rubber sheet in an electric field, and found that this change in thickness, the modulus of elasticity, and the difference in potential were quantitatively related to each other. (*See* also pp. 394 and 398.) Corresponding investigations [229] were carried out on glass, paraffin, and ebonite.

The sheets of rubber studied were of vulcanized, Para rubber, free from fillers; when pure, unvulcanized rubber was used, there was a marked permanent set. With a sheet of 0.35 cm. thickness, a shrinkage of thickness of $\Delta e = 4.5 \times 10^{-6}$ cm. was caused by a potential difference of 16.4 electrostatic units, the shrinkage for 38.3 electrostatic units being 22.5×10^{-6} cm. These changes in thickness correspond to within 2×10^{-6} cm. with the theoretical calculations made from the following relation between Δe, the shrinkage; E, the Young's modulus; ϵ, the dielectric constant; and V, the potential difference:[230] (*See* p. 394.)

$$\Delta e = \frac{1}{E} \cdot \frac{\epsilon V^2}{8 \pi e}$$

Piezo-electric investigations on ebonite, vulcanized soft rubber, glass, horn, etc., were made by K. R. Brain,[231] who was able to study the behavior of electric charges of the same order of magnitude as those to which Curie had

[226] K. Geisler, "Künstlicher Kautschuk für elektrische Isolierungszwecke," Verlag des Vereines deutscher Ingenieure, J. Springer, Berlin, **1922.**

[227] Compare Günther-Schulze, "Über die dielektrische Festigkeit," p. 112, J. Kosel und F. Pustet, Kempten, **1924,** and Figs. 33 and 34.

[228] *Compt. rend.*, **163,** 169, 479 (1916).

[229] The earlier investigations of observers on glass furnished the starting point for these experiments. A. Righi, *Mem. accad. Bologna,* (3), **10,** 407 (1879); also G. Quincke, *Wied. Ann.*, **10,** 161 (1880); **19,** 705 (1883), as well as Cantone and Sozzani, *Rendic. ist lombardo sci.,* (2), **33,** 1059 (1900)—"Electrostriction."

[230] All the factors in this equation are to be expressed in the c. g. s. system. The modulus of elasticity given on p. 438 in kg. weight per mm.^{2} units, must be changed over to the absolute system by multiplication by 9.81×10^7. The reciprocal of Young's modulus, $1/E = \alpha$, in the above example has the value 2.8×10^{-8} dynes/cm.^{2}. The absolute electrostatic unit of potential has the value of 300 volts. The unit of length is the centimeter.

[231] *Proc. Phys. Soc. (London),* **36,** 81-93 (1924).

subjected crystals. For small loads, the charge was found to be proportional to the load, but for larger loads, the charge increased more slowly. Hysteresis and fatigue phenomena were also observed. Cubical test pieces of milled stock for insulation purposes and other types of rubber behaved in an anisotropic manner in relation to their piezo-electric effect.

Finally, there are some investigations in the realm of triboelectricity or contact electricity to be mentioned. P. E. Shaw,[232] established a triboelectric series, or sequence of various materials, such that the polarity of the electric charges resulting from mutual rubbing of these materials would be indicated by the relative positions of the materials in the series. This order can be very materially influenced by the temperature of test. H. F. Richards[233] made observations on the charge assumed by rubber when it was heavily pressed against hard materials whose dielectric constants varied from 2.8 to 7.8. He found the charge to be independent of the nature of these materials. (*See also* electrophoresis, p. 493.)

Magnetic experiments with rubber, in an attempt to prove its diamagnetic character, have not as yet been proposed. Such experiments might prove very useful for the study of the anisotropy of rubber. The author would like to reserve for himself the work of determining the magnetic susceptibility of rubber in connection with its dependence on the degree of extension.

Swelling and Solution of Rubber

Introduction

After S. Peal (1791) first noticed that raw rubber, which up to that time had been known only as the latex emulsion or in its solid coagulated form, had the ability to swell in turpentine, and finally to go into solution, an extensive field of technical usefulness was foreseen for rubber. A long time elapsed, however, before this usefulness could be exploited in a practical manner, as a suitable and volatile solvent was not immediately at hand. When benzene became available as a product of the destructive distillation of coal, an excellent solvent was recognized in it by Macintosh (1823). Later this substance was displaced by benzine as a solvent for rubber. However, we are here interested in the process of solution of rubber more from the standpoint of its general physico-chemical aspects, than from that of its technical utilization.[234]

It is not surprising, considering the long time during which the manufacture of rubber goods has developed in a purely empirical way, and also with an unusual degree of secrecy, that no proper study has been considered of the processes of swelling and solution of rubber. Theoretical insight into this field has come only recently.

If we classify gels, as did Freundlich,[235] into those which swell and exhibit elasticity and those which do neither, then rubber gels fall in the first class. This group is characterized by the fact that the absorption of liquid causes a very considerable increase in volume, while drying of the gel causes a con-

[232] *Proc. Roy. Soc. (London)*, **A 94**, 16-33 (1918); the author uses the expression "triboelectricity," which may be suitably applied to some types of experimental technique.

[233] *Phys. Rev.*, (2), **22**, 122-123 (1923).

[234] The following references treat the technological aspect of solvents for rubber: A. Aufrecht and F. Jacobsohn, *Gummi-Ztg.*, **24**, 1755, 1789, 1826, 1857 (1910); D. F. Twiss, *India Rubber J.*, **74**, 573, 739, 773 (1927).

[235] H. Freundlich, "Kapillarchemie," 3rd Ed., Akadem. Verlags-Ges., Leipzig, **1923**; "Colloid and Capillary Chemistry" (translated from the third German Ed. by H. S. Hatfield), p. 662, E. P. Dutton, New York, **1926**.

stant decrease in volume, until finally a thick, cohesive mass remains, which is apparently entirely free from porosity. On account of this, the elastic gels, in contrast to the inelastic, of which the commonest example is silicic acid, behave in an entirely selective manner in the presence of a new supply of liquid. They do not absorb any and all liquids, but give evidences of swelling only under the influence of specific liquids, so that different substances actually exhibit quite specific swelling properties.[236] By this means a final state can be reached which is more or less similar to a solution; or definitely limited swelling can exist, in which case, the taking up of the swelling agent can reach only a certain maximum amount. Between these last-mentioned extremes, there are many intermediate conditions possible, in which, as in the case of rubber with increasing swelling, a certain fraction of the material may pass into the state of solution, though none of this material may be truly in the molecular form.

If, however, all violent agitation of the swelling specimen in the liquid is avoided, it is possible to count rubber in the class of substances of limited swelling power, somewhat in the same category as gum arabic.[237] Accordingly, the swelling ability of rubber with different swelling agents has been made the subject of repeated experimental study.[238]

Experimenters have tried to draw conclusions as to the structure of rubber from the phenomena which appear during swelling and solution of rubber, using the widest possible variety of viewpoints.* In the final analysis, the fractionation experiments owe their origin to these observations, which in Pummerer's hands led to the purification of the rubber hydrocarbon (*see* p. 166). This is a particularly opportune time to mention the experiments of P. Bary,[239] who sought to find some new information from a study of the process of solution. In contrast with the two-phase theory of rubber, which was previously discussed (*see* p. 423), Bary introduced a theory of solid solution, in which the various polymerization products of the iso-colloidal rubber exist together. The rubber structure is thus built up of interlaced chains, which are broken apart by the process of swelling and also by mastication. There is also a noticeable change in the degree of aggregation with time as manifested in the fractionated solution of rubber, as it was investigated by B. Caspari and Feuchter, for instance (*see* p. 423). This viewpoint will again be encountered in later discussion.

Swelling Pressure and its Determination

Although rubber increases its volume enormously in swelling, the total volume of the swelling system decreases slightly. After G. Flusin[240] pub-

[236] *Cf.* the earlier statement concerning the reciprocal action between the swelling substance and the swelling agent; p. 433 of this text, footnote.

[237] The processes which occur under different conditions have become better known through the work on the fractional solution of rubber by Caspari, Feuchter, and especially by Pummerer. (See p. 174 of this text.)

[238] Observation added during proof-reading: Special emphasis should be laid on the recent special issue of the Kolloid-Zeitschrift, "Gallerten und Gele," edited by Wolfgang Ostwald, in which the general viewpoints are considered. *Kolloid-Z.*, **46**, 241-368 (1928). See also the section on swelling, by J. R. Katz, in K. Hess, "Chemie der Cellulose," Leipzig, **1928**.

* Translator's Note. A practical application of the influence of a swelling agent on the fundamental relation existing between the temperature of retraction of a cured rubber strip and its "state of cure" (or vulcanization coefficient) has been made by R. H. Gerke in the so-called "T-50 Test" for state of cure. (For further details of this test, *see* p. 552.) —N. J.

[239] *Rev. gén. caoutchouc*, **2**, No. 20, 5-9, (1926); No. 21, 3-7 (1926); P. Bary and E. Fleurent, *Compt. rend.*, **184**, 947-8 (1927).

See also the general review of structural studies of rubber by P. Bary and E. A. Hauser, *Rev. gén. caoutchouc*, **5**, No. 42, 3. (June 1928). See also *Kautschuk*, **4**, 96-102 (1928).

[240] *Ann. chim. phys.*, (8), **13**, 488 (1908)

lished some data on rubber, in connection with his observations on the swelling power of various substances, E. Posnjak [241] at the instigation of Freundlich, undertook a fundamental investigation of the swelling pressure of rubber. These measurements have been extensively discussed from the theoretical standpoint. If a resistance is placed against the increase in volume of swelling rubber, the swelling continues and the resisting force is overcome by the swelling force of the rubber. However, this swelling force is not infinite, and its value can be determined if the resisting force is so far increased that no further swelling of the rubber is ascertainable. Then a point is reached at which any further increase in the resisting force causes some of the swelling agent to be pressed out of the gel. There is, therefore, a thermodynamic equilibrium, in which the absorption of a given amount of swelling agent corresponds to a certain pressure.

For making measurements of the swelling pressures of raw rubber and also of gelatin, Posnjak used a glass tube, on whose lower end was cemented a clay cup (*see* Fig. 97). If a small piece of raw rubber, say 0.0667 gram of

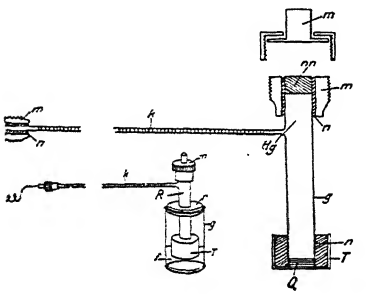


Figure 97—Apparatus for measurement of swelling pressure.
(According to Posnjak.)

Left: Assembly view of apparatus.
Right: Section through the swelling tube.

m screw connection for manometer.
n cement.
nn sealing compound (wax, rosin).
k graduated glass capillary.
Hg mercury.
g glass tube.
T clay cup.
Q sample of material being swollen.
R glass tube.
g vessel containing swelling agent.
f liquid (swelling agent).
r cork.

Para rubber, is placed in the bottom of the glass tube of 12 to 14 mm. diameter, and the whole is then immersed in a beaker of benzene, the benzene diffuses through the porous clay cup to the rubber. In order to measure both the volume of solvent absorbed and also the pressure caused by the swelling, the open glass tube above the rubber sample is filled entirely with mercury, which extends into a visible calibrated capillary side tube, so that from the movement of the meniscus the volume of fluid absorbed can be computed. The resisting pressure may be obtained from compressed air which is manometrically measured, and which acts against the same mercury meniscus. With this measuring apparatus, Posnjak investigated the swelling of rubber in numerous organic liquids, and found that the pressure became constant in the course of a few days. This was taken as a good indication that equilibrium had been reached. In order to obtain a relation between the volume of swelling agent absorbed and the corresponding pressure, it is necessary to hold the temperature constant and to make certain that the mercury meniscus is stationary, before reading the volume and the pressure. Using as the unit of measurement of the degree of swelling, the concentration c of the original dry gel (grams of dry gel per 1000 cc. of the total volume), and further neglecting the slight shrinkage that takes place during swelling, the relation between the swelling pressure P and the concentration c may be simply ex-

[241] *Kolloidchem. Beihefte*, **3**, 417 (1912). The theoretical considerations of Freundlich are given here in conjunction with the experimental data of Posnjak.

pressed by the following equation, which was derived by Freundlich:

$$\log P = \log P_0 + k \log c \qquad (25).$$

where P_0 and k represent constants. The proportionality factor P_0 may be recognized as the pressure which exists at a concentration equal to 1.

Table 10 contains a proof of the validity of equation (25). The weight of the sample of rubber used was 0.0667 gram. The results agree with the equation very well, as is shown by the agreement between the observed and calculated values, using as constants $P_0 = 0.00044$ and $k = 2.88$.

TABLE 10.—*Swelling of Raw Rubber in Benzene. (According to Posnjak).*

P gram/cm.^{2}	c Observed	c Calculated
720	144.6	143.8
1120	164.2	167.6
2120	208.1	209.1
3120	240.0	239.2
5120	289.4	284.1

Figure 98 gives the linear relation (which may be derived from the equation) between log P and log c for ten different organic swelling agents. In

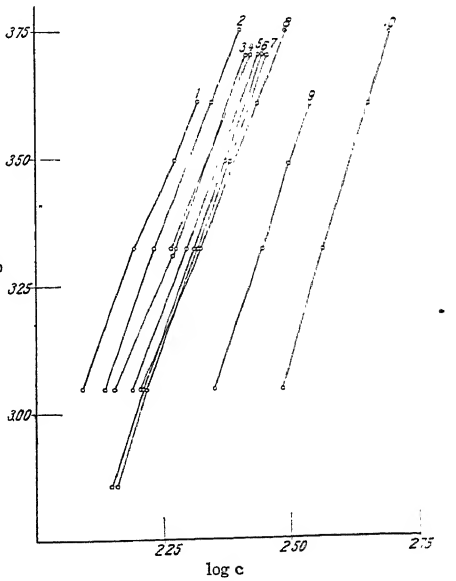


Figure 98—Dependence of the swelling pressure, P (in g./cm.^{2}), on the concentration of the gel, c (g. rubber per 1,000 cc. of gel.)
(According to Freundlich and Posnjak.)

The curves refer to the following swelling agents:

1. Carbon tetrachloride $P_0 = 566 \times 10^{-5}$; $K = 2.53$
2. Chloroform $P_0 = 265 \times 10^{-5}$; $K = 2.64$
3. Acetylene dichloride $P_0 = 472 \times 10^{-5}$; $K = 2.48$
4. Tetrachlorethane $K = 2.86$
5. Toluene $P_0 = 280 \times 10^{-5}$; $K = 2.56$
6. Thiophene $P_0 = 26.7 \times 10^{-5}$; $K = 2.98$
7. Benzene $P_0 = 44 \times 10^{-5}$; $K = 2.88$
8. Cymene $P_0 = 367 \times 10^{-5}$; $K = 2.48$
9. Ethyl ether $P_0 = 9.2 \times 10^{-3}$; $K = 3.01$
10. Ethylene chloride $P_0 = 0.58 \times 10^{-5}$; $K = 3.33$

contrast with the constant P_0, the exponent k is only slightly dependent on the liquid used. Since this exponent is characteristic of the slope of the curves, and since these curves are all approximately parallel, an average value for the exponent k, may be taken as 2.7.

The equation (25) may be derived with the assumption that, in each stage of the swelling process, the relative change in pressure is proportional to the

relative change in concentration, which is expressed by the following differential equation:

$$\frac{dP}{P} = k\frac{dc}{c}, \tag{26}$$

which in integral form is: $\log P = k \log c + \text{const.}$

Now, since for $c = 1$, $\log P_0 = \text{const.}$, we have:

$$\log P = k \log c + \log P_0 \qquad P = P_0 c^k.$$

In the case of rubber swelling in benzene, the contraction [242] is quite insignificant. Its determination is attended with uncertainty, but the value has been obtained by Posnjak from measurements of the density of the rubber before swelling and during swelling. His results are summarized in Table 11:

TABLE 11.—*Contraction of Volume of Unvulcanized Rubber during Swelling in Benzene (According to Posnjak).*

Amount of liquid absorbed, per cent	Observed volume	Calculated volume	Contraction
34.2	1.091	1.099	0.008
68.8	1.096	1.106	0.010
97.9	1.101	1.110	0.009

THE RATE OF SWELLING

Posnjak measured also the rate of swelling, i.e., the speed with which equilibrium was reached. Among other things, he observed that one-half year of natural aging of the rubber did not materially affect its rate of swelling. Posnjak was able to formulate the rate of swelling after the manner of a first order chemical reaction, and found the results to be in good agreement with the equation:[243]

$$k = \frac{1}{t_x} \log \frac{W}{W_\infty - W_x} \tag{26a}$$

In this equation, k is the reaction rate constant, W_x and W_∞ are the absorbed fluid masses at time t_x and at equilibrium, respectively. For example, raw rubber, swelling in benzene at 18° C. with an external pressure of 1120 gram/cm^2., absorbed at saturation a weight of benzene $W_\infty = 0.3337$. The constant $k = 0.0020$ was determined from the values $t_1 = 145'$, $t_2 = 1185'$, $t_3 = 1840'$, and the corresponding figures for the weights of benzene absorbed; $W_1 = 0.0905$ gram, $W_2 = 0.3002$ gram, $W_3 = 0.3194$ gram. In chloroform, at 17° C., but under otherwise exactly the same conditions, the reaction rate constant was $k = 0.00057$. Similar kinetic studies were made by Flusin [244] on vulcanized rubber.

[242] In this connection an article has appeared on the change in total volume during the formation of rubber sols: W. A. Gibbons and Eardley Hazell, *J. Am. Chem. Soc.*, **49**, 620 (1927).

[243] Concerning the kinetics of heterogeneous systems, see pp. 440 and 464 of the text by J. Eggert, mentioned on p. 413.

[244] D. Spence and G. D. Kratz [*Kolloid-Z.*, **15**, 217-226 (1914)] published their observations regarding the swelling of rubber in organic liquids, and purposely avoided any mathematical treatment of the data. In a study of osmosis and the swelling of disperse systems, Wolfgang Ostwald and K. Mündler have generalized the formulation of Freundlich and Posnjak [*Kolloid-Z.*, **24**, 7-27 (1919)].

In connection with the figures obtained by Flusin [244a] for the rate of solution of a swelling agent in rubber, P. Bary [245] made the following calculations, which differ from those given above:

$$p = \frac{tp_s}{A + t} \qquad (26b)$$

In this equation, p refers to the weight of liquid held in unit weight of the gel, and p_s to the same for the condition of saturation, when t approaches infinite values; A is a constant which depends on the conditions of the experiment, but which is strongly influenced by the strength of the rubber plate being used.

Bary found good experimental verification of equation (26b), as the following tabulation shows:

t in min.	Volume in cc.	p Observed	p Calculated	Difference p (calc.) $-$ p (obs.)
1	64.9	0.456	0.436	$-$ 0.020
5	233	0.751	0.751	0.000
15	445	0.852	0.853	0.001
30	602	0.885	0.883	$-$ 0.002
60	724	0.904	0.900	$-$ 0.004
180	778	0.910	0.910	0.000
1440	811	0.913	0.915	0.002

These data were taken from the work of Flusin on the swelling of vulcanized rubber in carbon bisulfide. The rubber was used in the form of thin plates, of about 1.33 mm. thickness, and contained 1.28 per cent combined sulfur and approximately 2 per cent ash. The results of the measurements were calculated in terms of the liquid volume in cc. absorbed per 100 g. of rubber. The constant A in the equation (26b) (above) has the value 1.1 in this example, and the constant p_s the value 916. Other examples of the values of these constants are as follows: for chloroform $A = 1.7$, $p_s = 0.940$; and with toluene: $A = 3.6$, $p_s = 0.870$; with acetone, the values: 226 and 0.123; with ethyl alcohol: 509 and 0.0267; and finally, with water: 3830 and 0.0180.

To represent the rate of swelling v, as exemplified by the data of Flusin, Bary found the equation:[245a]

$$v = B\,(p_s - p)^2 \qquad (26c)$$

which does not correspond to the rate which is to be expected from the theory of Nernst, Noyes, Whitney [246] and others, according to which, for example, the rate of solubility of benzoic acid in water is proportional at any time to the difference between the existing concentration and the concentration at

[244a] *. chim. phys.*, (8), **13**, 488 (1908).

[245] *Compt. rend.*, **161**, 589-591 (1915).

[245a] By differentiation of equation (26b), we obtain equation (26c), if in the resulting expression t is substituted for the value $\frac{pA}{p_s - p}$, conformably with equation (26b). The equation then reads: $v = \frac{dp}{dt} = \frac{(p_s - p)^2}{Ap_s}$. It is to be noted that this expression for the rate of swelling of rubber differs from that found by Freundlich and Posnjak, since equation (26a) in differential form reads: $v = \frac{dw}{dt} = k\,(W\infty - Wx)$, or, in a form analogous to that of equation (26c): $v = B\,(p_s - p)$. The quadratic function results from work with vulcanized rubber, and the linear relation of Posnjak results from work with lamellae of raw Para rubber. If the difference between the differential equations for these two cases is not to be ascribed to the difference between the materials, then it must be sought in differences in technique. Obviously, the difference is in need of an explanation. *See also* the discussion following equation (26c).

[246] *Z. phys. Chem.*, **1**, 209 (1887); *J. Am. Chem. Soc.*, **19**, 930 (1897), and also *Z. phys. Chem.*, **23**, 689 (1897); **35**, 283 (1900); **47**, 52, 56 (1904).

saturation. According to Bary,[247] differences in the swelling of rubber samples may be ascribed to differences in the mechanism involved. The secondary bonds between the long chains are loosened, and the freed valences are saturated in accordance with their affinities.*

Finally in this connection, there must be mentioned a case of thermolysis (Ludwig-Soret-phenomenon) which was studied from the standpoint of its application to rubber, in the laboratory of Tammann, by H. Wessel.[248] He determined among other things, the pressure-concentration, or p, c-curve for rubber shreds which had been washed with benzene vapor of known partial pressure, and which had therefore taken up benzene to a concentration c. If a sample of rubber saturated with benzene vapor is placed in a closed glass tube and a temperature gradient is then established, liquid benzene will appear at the cold end of the tube (*see* p. 479, footnote 253).

Heat of Swelling and Solution

It should be noted that heat of swelling and solution (*see* p. 436 and p. 463), is a complex phenomenon, in which it is necessary to differentiate between the heat of adsorption which appears at the moment of wetting, and the total heat of swelling or solution. It is difficult to determine these heats separately (*compare* with the considerations in footnote 253 of p. 479). So long as experiments are carried out with ordinary, rather than carefully purified rubber, such distinction by separate experiment had best not be attempted, until results can be obtained that are free from objection. It is reasonable to assume that after further progress, a swelling process which is nearly complete will not show any such considerable heat effect as appears at the beginning of the process, where the forces between the micelles must be overcome by the swelling agent. From a practical standpoint, therefore, the heat of swelling is given off and may be determined without serious error in a short time after the beginning of the process long before the swelling is complete. If the total heat effect is negative, that is, if the swelling has taken place with an attendant cooling, then there may be expected an adsorption of an exothermic nature at the moment when the vapor and the rubber surface come into contact. This thermal effect was noted as an actual experimental fact by A. S. Houghton,[249] who covered one junction of a thermocouple with a rubber film, and leaving the other bare, placed both junctions in an atmosphere of benzene, of ether, and of other vapors at the same temperature. In all cases the covered junction became warmer. In the case of ether, for example, there appeared a difference of temperature of 1° C.; with benzene and pyridine, about 0.3 to 0.4° C.; and with other vapors considerably less. If after the temperatures of the two junctions had become equal, they were placed in a vessel filled with charcoal, so that the vapors were again absorbed from the rubber, a cooling always followed. In agreement with these results, F. Hartner observed in his experiments, in which he was able to determine the swelling heat alone, that in the first few moments of contact of the swelling agent with the rubber, heat was generated, but that soon the stronger cooling effect of the swelling was predominant.

[247] *Rev. gén. caoutchouc*, **3**, No. 26, 5-8 (1926); *Gummi-Ztg.*, **40**, 2206 (1926).

* Translator's Note. The rate of swelling of several specimens of ebonite in benzene in the dark at 34° C. has been studied by B. D. Porritt and J. R. Scott [*India Rubber J.*, **86**, 253 (1933)]. Some specimens were found to crack very badly on swelling. Those samples which did not crack showed the swelling maximum to decrease with increasing vulcanization coefficient, and the time required to reach 0.1 of the maximum swelling to increase sharply with the vulcanization coefficient.—N. J.

[248] *Z. phys. Chem.*, **87**, 215 (1914).

[249] *Proc. Phys. Soc. (London)*, **35**, 39-44 (1923)

Recently H. Kroepelin [250] made a theoretical analysis of the heat of dilution of rubber solutions on the basis of thermodynamic considerations. He found that with the addition of 1 gram of benzene to a large mass of dilute solution of rubber in benzene, a heat of dilution of the order of 0.001 gram cal. was obtained.

The integral heat effect in the swelling and solution of rubber, as has been mentioned on p. 436, is greatly dependent on the age and condition of the rubber sample, and it is evident that the whole matter of the swelling of rubber is not as well understood as other swelling processes which are easier of theoretical approach. Conversely, however, these unusual phenomena allow conclusions to be drawn as to the structure of rubber and its changes with aging. For instance, Bary,[251] by noting the change in the benzene-soluble fraction of Para rubber after 15 years of natural aging, came to the conclusion that the degree of aggregation or polymerization must have increased during this time.

Maximum Swelling

The determination of the swelling maximum of rubber is comparatively easy. A weighed amount of the gel is placed in the liquid, and from time to time, after removing the adhering drops of unabsorbed liquid, the mass is weighed, until no further increase in weight occurs. By this means, Flusin determined incidentally, in his above-mentioned work, the ultimate swelling of vulcanized rubber.* The maximum swelling is greatly dependent on the chemical nature of the liquid used. F. Kirchhof [252] investigated in a systematic manner the swelling of vulcanized rubber, and noted a similar dependence on the degree of vulcanization of the rubber. He also carried out experiments on the swelling of rubber in vapors, and made observations on the rate of swelling under these conditions.[253]† Generally raw rubber reaches

[250] *Kolloid-Z.*, **47**, 294 (1929); the recent experiments of this author, to which we shall refer often in this chapter, unfortunately could not be treated more fully in the short time available before publication.

[251] *Compt. rend.*, **152**, 1386 (1911); and also *Rev. gén. caoutchouc*, **3**, No. 26, 5-8 (1926).

* Translator's Note. A new method has been devised by D. J. van Wijk [*Kautschuk*, **9**, 18 (1933); *Rubber Chem. Tech.*, **6**, 406 (1933)] for the determination of ultimate swelling. The apparatus, called a "Voluminometer," supersedes in accuracy, speed of operation, and simplicity all previously described apparatus, and allows swelling determinations to run over long periods of time without loss of accuracy of the final result. For details of the apparatus, manipulation and typical results, the reader is referred to the original publication.—N. J.

[252] *Kolloidchem. Beihefte*, **6**, 1 (1914).

[253] There are several articles published on the rate of swelling in vapors, but the conditions of the experiments are so poorly described, from the physical standpoint, that no theoretical significance can be attached to their results. If solid rubber takes up a liquid, the adsorption on the surface and the subsequent diffusion into the interior of the rubber must be differentiated. It would, however, seem difficult to consider these two processes separately. Attention must be given to another piece of work by St. Reiner [*Kautschuk*, **4**, 210 (1928)], which covers only a small period of the initial swelling process, one in which the rubber is still far from the maximum swelling condition. In the unvulcanized state, rubber is capable of taking up several hundred per cent of its own weight of swelling agent in the vapor form. Compare also with Wlček [*Gummi-Ztg.*, **43**, 310 (1928)]. The curve which the system rubber-vapor follows in equilibrium must represent a logarithmic decrease in rate of swelling with the time, and must terminate (inosculate) asymptotically parallel to the time axis; that is, it must be convex towards this axis. If in a given experiment this is not the case, the variation must be caused by disturbing circumstances, such as diffusion and convection streaming of the vapor to the further and deeper layers of the pile of rubber shreds, for example.

† Translator's Note. C. M. Blow and P. Stamberger [*Rec. trav. chim.*, **48**, 681 (1929); *Rubber Chem. Tech.*, **4**, 64 (1931)] discuss the influence of the amount of surplus of the swelling liquid on the swelling maximum of rubber. They found, in common with several other previous investigators, that the per cent swelling at maximum increases with the amount of swelling agent initially used. However, increasing this amount beyond a certain limit has practically no further effect on the swelling maximum. It is also noted that the swelling of rubber is less if there is some rubber dissolved in the swelling liquid. Although the mechanism is not entirely understood, this is believed to be largely an osmotic phenomenon.—N. J.

its swelling maximum much more rapidly than vulcanized rubber (in approximately 0.1 the time), although its capacity for absorbing the swelling agent is some two to three times as great as that of the latter. Naturally this relation does not apply to vulcanized rubber containing pigments.[254]*†

Wolfgang Ostwald[255] sought a relation between the ability to cause swelling of rubber and some characteristic physical constant of each individual liquid, and found a very noteworthy correspondence with the dielectric constant, ϵ. The greater the dielectric constant ϵ, the smaller is the ability, Q, of a liquid to swell rubber. In agreement with this discovery, water ($\epsilon = 81$) has very little swelling effect, while carbon bisulfide, ($\epsilon = 2.26$) is, in contrast, very effective. With certain notable exceptions, liquids have constants which can be related by an equation of the following form:

$$n\sqrt{Q\epsilon} = \text{const.}$$

in which the value of n varies from 2 to 3, and the numerical value of the constant depends on the unit of mass chosen for the expression of the variables. This equation suggests one of very similar nature by means of which Walden was able to express a relation for the solubility of several materials in a large number of organic liquids. Since the electrical polarity, which is used in the expression for the dipole moment of the molecule, has recently been recognized as being of importance in the interactions of materials, the relation between the ability to cause swelling and the dipole moment may perhaps be considered as of greater importance and more conclusive than heretofore.[256]

Later, LeBlanc and Kröger[257] published their opinion that the Ostwald relation holds only for a limited series of substances which are chemically similar, and illustrated their contention by means of a statistical survey, one of the results of which was that the introduction of sulfur or a halogen into a substance increased its ability to swell rubber. The rate at which a sample of rubber swells, according to their results, is strongly dependent at first on the viscosity of the swelling agent. Carbon bisulfide and mercaptans possess the power to swell rubber with enormous rapidity, as would be indicated by their great power of swelling and their low viscosity. Since, in these liquids, vulcanization proceeds only very slowly under the influence of such vulcanizing agents as sulfur chloride, for example, their special posi-

[254] Besides the investigations mentioned above, there are also the studies made by A. Dubosc on the ability of rubber to swell, in which numerous references are given to numerical data on the increase in weight, the increase in volume, the maximum swelling, and the time required for its attainment. *Caoutchouc & gutta-percha*, **16**, 9813, 9845, 9999 (1919). In a similar manner, F. Boiry investigated the capacity of vulcanized rubber for swelling, as dependent on the nature of the swelling agent; *Caoutchouc & gutta-percha*, **20**, 12.010 (1923).

* Translator's Note. Oil-resisting rubbers are discussed by W. J. S. Naunton, M. Jones, and W. F. Smith [*India Rubber J.*, **86**, 446 (1933)]. Since over-milling lowers oil resistance, latex compounds were tested and found more oil-resistant than milled compounds. Bromine water treatment of the surface of a soft rubber which is not subjected to mechanical deformation, makes it satisfactory for resisting oil. Synthetic rubbers, such as Duprene, are more resistant to oil swelling than are natural rubbers. A flexible, oil-resistant hard rubber can be produced by using a hard-cured mixture of Duprene in an ebonite-type rubber compound. A high cure with high sulfur content, and with liberal use of antioxidants, improves oil resistance. Magnesium carbonate as a filler lessens oil swelling.—N. J.

† Translator's Note. The relation between water absorption by rubber and the protein content is discussed by S. J. Skinner and T. J. Drakeley [*Trans. Inst. Rubber Ind.*, **7**, 196 (1931)], who find that in general, the moisture absorption increases with increasing protein content. The effects of the degree of shredding of the rubber, and of the relative humidity of the surrounding gaseous phase, are also discussed.—N. J.

[255] *Trans. Faraday Soc.*, **9**, 35 (1913); *Kolloid-Z.*, **29**, 100 (1921). Compare also Wolfgang Ostwald, "Die Welt der vernachlässigten Dimensionen," 267 ff., 9th and 10th Ed., Th. Steinkopff, Dresden and Leipzig, **1927**.

[256] Concerning the definition of the dipole moment, see the text by Eggert (see p. 413 of this book) pp. 11, 165 and 315.

[257] *Kolloid-Z.*, **33**, 168 (1923).

tion in the field of cold vulcanization arises from the combined action of a rapid swelling ability and a slow vulcanizing ability. Carbon tetrachloride is inferior to these substances in this respect, but always distinguishes itself in the slowness of the vulcanization process which it causes.

A recent examination of the swelling properties of a synthetic product μ-polychloroprene, a polymer of chloroprene, has been made by W. H. Carothers, I. Williams, A. M. Collins, and J. E. Kirby* [*J. Am. Chem. Soc.*, **53**, 4203 (1931); *Rubber Chem. Tech.*, **5**, 7 (1932)]. These authors find for this polymer active swelling ability in carbon tetrachloride, carbon disulphide, benzine, nitrobenzine, pyridine, ethyl acetate, and ether. Compared with natural rubber, this polymer swells very slowly and moderately in gasoline and lubricating oils.

The swelling properties of various polymers of bromoprene are discussed briefly by W. H. Carothers, J. E. Kirby, and A. M. Collins [*J. Am. Chem. Soc.*, **55**, 789 (1933); *Rubber Chem. Tech.*, **6**, 317 (1933)].

The resistance to swelling of μ-polychloroprene in oils is mentioned by O. M. Hayden and E. H. Krismann [*Ind. Eng. Chem.*, **25**, 1219 (1933)].

Rubber Solutions

From the swollen state, rubber may be transformed into the condition of a viscous solution by the addition of more liquid, especially with the help of shaking. The high viscosity of such a solution is in general not only a criterion of the technical high quality of the rubber used (though certainly not a reliable one!) but also is in large measure dependent on its prior treatment. On account of this fact, rubber technologists have for a long time paid particular attention to the matter of the viscosity of rubber solutions. The influence of this factor is noticeable particularly in the magnitude of the ultimate swelling, as was determined by Klein and Stamberger [258] in a systematic series of experiments on unmilled and "dead-milled" raw rubber. As a result of its long milling, the latter has lost the original high ability to swell and thus has a greater tendency to form a solution. In accordance with the concept of these experimenters previously mentioned, rubber is considered as possessing an inner framework or structure whose destruction by "dead-milling" injures its ability to swell. With this weakening of the cohesive forces, there arises an increased tendency to dissolve, because of which, however, the exact definition of the resulting solutions is very difficult. Although the heat of swelling of rubber has been found by L. Hock and L. Hartner [259] to be dependent on its age, and also to be a measure of its degree of aggregation, yet with rapidly repeated alternate swelling and drying, its value remains practically unaltered. However, after milling, aged rubber takes on again the value of the heat of swelling it had before aging. This gives a hint that in the light of our previous discussion of free and bound micelle forces (or "secondary valences"; p. 433), milling has been shown by the experiments of Klein and Stamberger to decrease the aggregation, thus freeing the micelle forces, and making them available for assisting the penetration of the swelling agent.

This explanation is possible on the basis of the aggregation theory of Harries as extended by LeBlanc and Kröger.[260] The uncertainty of the theoretical explanation of the swelling of rubber is, however, still so great that the experimental facts sought particularly for the development of the theory must be given more consideration than the theory. Moreover, a truly satis-

* Translator's note by N. J.

[258] *Kolloid-Z.*, **35**, 362 (1924). Compare also Fry and Porritt, p. 488 of this text.

[259] Compare L. Hock, *Z. Elektrochem.*, **34**, 662 (1928); and further, Fr. Hartner, Dissertation, Giessen, **1929**, and also p. 463 of this text.

[260] *Kolloid-Z.*, **37**, 205 (1926) and p. 431 of this text.

factory study of this matter cannot be undertaken until there is available for such work a sufficient quantity of pure rubber. When the properties of this material are known more accurately, the peculiarities of the technical products will be easier to understand.

In contrast with its solubility, is the ease of precipitation of rubber from its solutions, a property which is frequently used in the purification of rubber. Its flocculation from benzene solutions by means of alcohol and acetone plays a particularly important practical role. W. A. Caspari [261] has made a thorough study of the systems rubber-benzene-alcohol and rubber-benzene-acetone. He finds that at 20° C. an almost complete separation of rubber from its benzene solution occurs when 80 volumes of anhydrous acetone, or 43 volumes of absolute alcohol, are added to 100 volumes of benzene. With increasing temperature, the ease of precipitation decreases markedly.

On the other hand, rubber can be used as a protective colloid for unstable colloids. For instance, E. W. Lewis and H. Waumsley [262] have prepared colloidal lead sulfide sols in benzene rubber solutions.

Similarly, F. Evers,[263] by reduction of a dilute solution of rubber in benzene under pressure, and in the presence of finely divided platinum, has obtained highly disperse platinum sols, from which the platinum and rubber were precipitated together, mainly on the anode, by the application of a potential of 40,000 volts per cm. (*Cf.* with electrophoresis, p. 493). The precipitated platinum was easily peptized.

Viscosity

The determination of the viscosity of rubber solutions will now be considered. In this study, also, it is preferable to use rubber in its purest raw form. Here also attention must be paid to the resins, proteins, and other serum substances, to see that they have no effect on the results. In this respect, technically important determinations were made by Eggink and de Vries,[264] who investigated the effect of additions of acid to benzene solutions, and G. S. Whitby [265] who studied the effect on the viscosity, of the addition of small quantities of organic bases and acids, and also of rubber resins, ammonia, etc. Whitby was able to demonstrate a striking decrease in activity of certain organic bases, notably piperidine, in the presence of rubber. The observation had been made several years before, both by G. Bernstein [266] and by F. Kirchhof [267] that small additions of sulfur chloride and of hydrogen chloride caused marked decreases in the viscosity of rubber solutions. Through reaction and adsorption of these additions, the micelle forces will obviously be utilized, so that their action on adjacent micelles is considerably diminished, a decreased viscosity thus resulting. As is to be expected, the previous treatment of the rubber, as in milling, etc., is not without effect on the viscosity of its solutions, as this also changes the micelle forces. H. R. Kruyt and W. A. N. Eggink [268] studied the effect on the viscosity of benzol

[261] *J. Chem. Soc.*, **107**, 162 (1915).

[262] *J. Soc. Chem. Ind.*, **31**, 518 (1912) and also *Kolloid-Z.*, **11**, 39-41 (1912) and *ibid.*, **40**, 139 (1926). In the latter reference, F. Haurowitz recommends a so-called "repair solution" as a protective colloid in the preparation of stable metal sols in benzene. See further *Chem. Zentr.*, **2**, 103 (1913). There have been patent advertisements concerning the electrical atomization of metals in hydrocarbons to which have been added small quantities of rubber.

[263] *Kolloid-Z.*, **36**, 206 (1925).

[264] W. A. N. Eggink, *Rec. trav. chim.*, **42**, 317 (1932). O. de Vries, *India Rubber J.*, **67**, 849 (1924).

[265] *India Rubber World*, **70**, 795 (1924).

[266] *Kolloid-Z.*, **12**, 273 (1913).

[267] *Kolloid-Z.*, **14**, 38 (1914).

[268] *Koninkl. Akad. Wetensch. Amsterdam, Wisk. Natk. Afd.*, **32**, 8-13 (1923). See also *Chem. Zentr.*, **94**, IV, 115 (1923).

solutions of rubber of the addition of various electrolytes and found decreases in the following order: HCl, SO_2, H_2S, CH_3COOH, $HgCl_2$. With the addition of ammonia, there occurred at first an increase to a maximum and then a decrease. The effects of aromatic and aliphatic anions were also investigated. The authors recommended that in order to suppress the effect of the electrolytes which exist naturally in rubber, a practical comparison must be made of the viscosities of several rubber solutions to which electrolytes have been added intentionally.

In an investigation of the effect of the solvent on the viscosity of rubber solutions, F. Kirchhof [269] was able to show that differences in the viscosity of the solutions indicated also differences in the ability of the solvent to swell rubber. It was shown by Emil Hatschek [270] that the stronger the swelling action, the higher was the viscosity of the sol formed in the same solvent.*

Even in the dissolved state, the rubber particle consists of a sheath filled with molecules of the liquid phase of rubber. Thus Einstein's equation fails to hold when applied to rubber in an attempt to find the relation between the inner friction and the concentration of the solution. This equation applies to lyophobic sols. P. Bary [271] attempted to make the equation applicable also to lyophillic sols. In its original form, the equation read:

$$\eta = \eta_0 (1 + 2.5v) \qquad (26d)$$

which states that the inner friction η of a sol may be calculated from that of the solvent, η_0, if v denotes the volume of suspended matter per unit of volume of the solvent. It will be noticed that the inner friction, as defined by this equation, does not depend on the degree of dispersion of the solid; yet the swelling of the particles of rubber due to solvation is not considered. If we assume that the volume v_0 of the dry colloid acquires a volume v through the process of solvation, where

$$v = v_0 (1 + a),$$

according to P. Bary's formulation, the equation (26d) reads

$$\eta = \eta_0 [1 + 2.5 v_0 (1 + a)]$$

Transforming this relation to that for relative viscosities, η', and placing η_0 equal to unity, the solvation factor may be expressed as in equation (26e):

$$a = \frac{\eta' - 1 - 2.5 v_0}{2.5 v_0} \qquad (26e)$$

In the transition to very dilute solutions, Bary [272] found that the limiting value for a with increasing dilution was zero. Of course a solvation equilibrium depending on the concentration must be assumed. The quantity a, which is

[269] *Kolloid-Z.*, **15**, 30 (1914).

[270] *J. Phys. Chem.*, **31**, 383 (1927).

* Translator's Note. Variations of viscosity with the solvent, the type of rubber used, the atmosphere and with irradiation of the solution, are discussed in a brief article by B. Dogadkin and M. Lawrenko [*Kautschuk*, **9**, 97 (1933); *Rubber Chem. Tech.*, **6**, 436 (1933)]. These experimenters found that between the temperatures of 0° C. and 50° C., the viscosity (relative to the pure solvent) of rubber solutions in benzene and xylene with less than 0.3 per cent rubber, is invariant with the temperature. For solutions between 0.3 per cent and 10 per cent rubber content, the viscosity of these solutions decreases linearly with the temperature, within these same limits. The deduction from these observations is that for low concentrations, the solution is truly molecular; for intermediate concentrations, the solutions contain micelles of rubber, and at higher concentrations, there is a continuous rubber phase present in the solution. Irradiation of a 1.0 per cent solution of pale crepe in xylene decreased the relative viscosity to a value corresponding to that for a 0.1 per cent solution which had not been irradiated.—N. J.

[271] *Compt. rend.*, **170**, 1388 (1920).

[272] This statement applies to such solutions as that of rubber in benzene, for example. In the case of gelatin sols, this behavior of a is not found. In Bary's language, a is the "Coefficient de gonflement." See also Wolfgang Ostwald, *Kolloid-Z.*, **23**, 68 (1918).

supposedly proportional to the total solvation of the dissolved material. Because the total solvation is unconditionally dependent on the size of the micelles, may be considered not only as a measure of the actual solvation, but also of the average particle size. Apparently there exists, besides the equilibrium depending on temperature and concentration, an equilibrium distribution between the existing particle sizes, somewhat in the sense of the theory of M. Volmer.[273] Thus there will always be a dependence of this distribution on the solvent.* Following these general considerations, we shall turn to the discussion of those investigations which deal with the practical determination of the viscosity of rubber solutions.

The first critical survey of the early literature on methods of determining the viscosity of rubber solutions was given by J. G. Fol.[274] From this survey the observations made with the Ostwald viscosimeter were considered the most dependable. Inasmuch as the viscosity changes to a considerable degree with the temperature and the concentration, the exact knowledge of these variables and their constancy throughout a given measurement of viscosity is of great importance. In order to obtain comparable results, Fol suggested that the rubber be cut into fine crumbs and dried over sulfuric acid in a vacuum desiccator, and that a known weight of it (say 0.250 g., 0.500 g., and 1.00 g.) be treated with 100 cc. of pure benzol. During three days, the swelling material in a brown glass vessel should be carefully shaken twice a day, and then filtered through glass wool. Four days after preparation, the solution, whose concentration is exactly determined by evaporation of the solvent, is subjected to a determination of viscosity in an Ostwald viscosimeter, preferably at a temperature of 30° C. From the time of efflux of the solution, the relative viscosity can be calculated. For this calculation, the time of efflux of the pure solvent is set as unity, and it must be noted that the choice of the solvent has a very considerable effect on this time of efflux. Various proposals have been made for the further mathematical evaluation of the results of this measurement.

Schidrowitz and Goldsbrough[275] showed the dependence of the relative viscosity on the concentration by means of a curve, whose form was considered characteristic of the viscosity of that material. They called the relative viscosity of the solution 2,000 times the slope of the viscosity curve at a concentration of 1 per cent. On the other hand, Fol decided to take as a measure of the viscosity the area between the curve and the concentration axis between 0 and 1 per cent concentration, terming this the "viscosity number" of the solution. After several discussions of the manner of designating relative viscosities, van Rossem[276] studied this matter on the basis of extensive data. He found that the viscosity curves for some 500 solutions of rubber in benzene did not cross one another when reduced to the same co-

[273] *Z. phys. Chem.*, **125**, 151 (1927).

* Translator's Note. The structural viscosity in the lyophilic sol, rubber, has been studied by W. Gallay [*Can. J. Research*, **7**, 671 (1932); *Rubber Chem. Tech.*, **6**, 371 (1933)] who finds that there are deviations from Poiseuille's law at all concentrations. The limiting concentrations above which structure becomes evident in the solution, and deviations from Poiseuille's law appear, agree with those calculated from Staudinger's equation [*Z. angew. Chem.*, **45**, 276, 292 (1932)] relating specific viscosity and molecular weight:

$$\frac{\eta_{sp.}}{c} = K M$$

where $\eta_{sp.}$ is the specific viscosity, c the concentration, M the molecular weight, and K a constant for any one series in the same solvent. Exposure to ultraviolet light was found to decrease considerably the viscosity of a sol of purified rubber.—N. J.

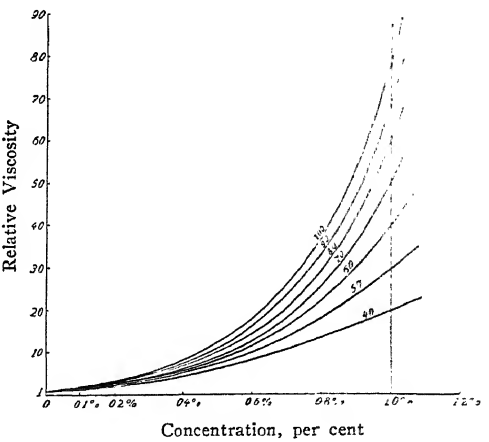
[274] *Kolloid-Z.*, **12**, 131-147 (1913). Compare also the earlier observations of Axelrod, *Gummi-Ztg.*, **19**, 1053 (1905); **20**, 105 (1905); also that of Eaton, *Gummi-Ztg.*, **27**, 2071 (1913).

[275] *J. Soc. Chem. Ind.*, **28**, 3 (1909).

[276] *Kolloidchem. Beihefte*, **10**, 83 (1918), in the extensive investigation entitled: "Untersuchungen des Niederlandischen Kautschuk Prüfungsamtes."

rdinates, as is shown in Figure 99. If we accept the material discussed by van Rossem, it will be found possible to obtain the "viscosity number" of Fol by a simple means. It is no longer necessary to determine the entire viscosity-concentration curve, but only to determine the viscosity of a given concentration below 1 per cent. From this value, plotted on the axis of Figure 99, it is possible to find directly, or by interpolation where necessary, the characteristic viscosity curve for the material in question, and with a simple measurement of the area under the curve through the point plotted, to find the "viscosity number" for the solution. For further particulars of this method, the original work of van Rossem should be consulted. It must be noted that in order to use this method, a viscosimeter of certain definite specifications must be available, in order that the curves of Figure 99 may be used directly.[277] It is important to exclude bright daylight during this work as the viscosity decreases considerably in its presence.

Besides the practical significance, there is considerable theoretical value in the method of van Rossem for the easy determination of the viscosity of solutions. It is noteworthy that with the analogous behavior of all the curves in Figure 99, every single solution may be designated by a definite characteristic number which is represented by the ordinate of the curve at a concentration of 1 per cent for the solution in question. In connection with Bary's analytical development of the concentration function, which was men-



Concentration, per cent

Figure 99—The most probable viscosity curves.
(According to A. van Rossem.)
The curves are designated by their respective viscosity numbers.)

tioned above, it would seem possible to characterize the viscosity of a rubber solution by the numerical value of a constant appearing in an algebraic equation, such constant being theoretically closely related to the size and degree of solvation of the micelles. Considered from the standpoint of molecular theory, these latter factors determine the course of the viscosity curve.

[277] K. Gorter, Department vom Landbouw Nijverheid en Handel, Mededeelingen over Rubber, No. 4, **1915**, and also *Chem. Abstracts*, **10**, 2541 (1916) did not accept the method of Fol but described another method. R. Gaunt [*J. Soc. Chem. Ind.*, **33**, 446 (1914)] followed the procedure recommended by Fol, in investigating the effect on the viscosity, of the type of rubber, of the solvent, and of variations of temperature, light, etc. In this work, he found the equation of Arrhenius [*Z. phys. Chem.*, **1**, 287 (1887)] to be satisfied approximately. If η is the viscosity at a concentration x, and k is a constant, this equation reads:

$$\eta = k^x$$

and can be represented by a straight line on semi-logarithmic co-ordinates, in which the abscissa is x, and the ordinate is log η.

The measurements just mentioned are always carried out under definite standardized conditions. However, as soon as valid general relations between the viscosity of a solution and the fundamental properties of its component parts is sought, the work cannot be restricted to definite standards. If the pressure which forces the solutions through the viscosimeter capillary is changed according to the law of Poiseuille, then the calculations yield viscosity values dependent on the pressure. This anomalous behavior of rubber solutions, which has already been noted by F. Kirchhof,[278] and which manifests itself also in a dependence of the viscosity on the radius of the capillary used, as noted by E. Hatschek[279] and also by Wolfgang Ostwald,[280] was recently made the subject of a detailed study by H. Kroepelin.[281] The results of this study have by now provided an exact foundation for the discussion of the measurements of viscosity of solutions of anomalous behavior. If the relative viscosity is considered as being dependent on the velocity gradients of the streaming liquid, it is found to be a linear function of the logarithm of these gradients. This relationship can be confirmed in the majority of rubber solutions. Should attention then be drawn to the pressure and the radius of the capillary, by the comparison of various experiments, these quantities cannot be placed directly in the Poiseuille equation and care must be taken to compare with each other only those relative viscosities which possess the same average velocity gradients.

In a less general form, the effect of pressure on the viscosity of rubber solutions was studied by W. H. Herschel and R. Bulkley,[282] who set up an empirical formula which was found to hold for solutions of rubber content varying from 0.1 per cent to 1.2 per cent.

TABLE 12.—*Dependence of the Viscosity of Rubber Solutions on the Temperature (according to LeBlanc and Kröger).*

Experimental Material: 1.5% rubber sols in carbon bisulfide. Time required for the pure solvent CS_2 to flow through the Ostwald Viscosimeter at 15° C.: 7 seconds.

Crepe rubber		Para rubber	
Temp. ° C.	Time Sec.	Temp. ° C.	Time Sec.
15	49.4	15	37.4
3	53.8	— 9	44.0
— 11	59.4	— 27	58.5
— 24	77.0	— 48	134.0
— 37	1605.0	— 53	gel

Investigations on the effect of low temperatures on the viscosity of rubber solutions have been made by M. LeBlanc and M. Kröger,[283] who showed that because of increasing aggregation at the lower temperatures, these solutions change over into a gelatinous mass, somewhat in the same way as though they had been vulcanized in sulfur-chloride. It is possible to obtain in solution a "cold vulcanization"—albeit a reversible one—such as we have already seen in raw rubber. From a quantitative standpoint, this phenomenon is highly dependent on the quality or variety of rubber used. In Table 12 above are given the observations on solutions of crepe and hard cure Para. (*See* p. 428.)

[278] *Kolloid-Z.*, **15**, 31 (1914).

[279] *Kolloid-Z.*, **13**, 95 (1913).

[280] *Kolloid-Z.*, **46**, 136 (1928).

[281] *Kolloid-Z.*, **47**, 294 (1929). This work could not be mentioned until the proof of the present book was ready; hence the brief note.

[282] The viscosimeter used in this work was that of Ostwald or Bingham, *Kolloid-Z.*, **39**, 291 (1926).

[283] *Kolloid-Z.*, **37**, 212 (1925), and *Z. Elektrochem.*, **27**, 335 (1921). In this latter work, the authors ascertained the relation between viscosity and vulcanization coefficient in solutions of vulcanized rubber.

The method described above for measuring the viscosity of rubber solutions by means of the capillary tube fails, however, as soon as the measurements involved concentrated sols. In this field the method of the slowly falling ball, treated mathematically by Stokes,[284] has been conveniently used by various authors. Recently, Abernethy[285] has described a falling-ball viscosimeter which can be calibrated in c.g.s. units, and with which benzene solutions containing up to 40 per cent by weight of rubber can be satisfactorily handled.

Recently B. A. Jones* [*Ind. Eng. Chem., Anal. Ed.*, **6**, 80 (1934)] has developed a useful adaptation of the falling sphere viscometer for routine control work, which gives measurements in seconds numerically approximating viscosity in poises.

The falling sphere type of viscometer has been so altered in such a way that reliable measurements of the consistency of rubber cement may be obtained automatically. The instrument consists of a highly polished steel guide, rigidly clamped at an arbitrarily-chosen angle of 75° from the horizontal. Along this guide a ⅜″ steel ball is allowed to fall under its own weight, through a sample of the rubber cement to be tested. The time required for the steel ball to fall along the guide for an arbitrarily-fixed distance of approximately 12″ is taken as a measure of the consistency of the rubber cement. The measurement of the time is accomplished automatically by means of a simple application of a Grid Glow (glow discharge) tube, as follows: the steel ball is first held by an electromagnet at the top of the column of rubber cement, but under the surface thereof, and in electrical contact with both the guide and the pole of the electromagnet. In this position the ball, operating electrically through the Grid Glow tube and a high resistance relay, prevents an electric (Telechron) clock from starting. As soon as the operator, by decreasing the current through the electromagnet, allows the ball to leave the pole-piece, the electric clock commences to time the fall of the ball as it moves along the guide through the rubber cement. The electric clock is automatically stopped when the ball makes contact with an electrode at the lower end of the guide. Reliability of operation is ensured because of the extreme sensitivity of the Grid Glow tube to small changes in values of very high resistance.

This instrument has been shown to give reproducible results with a medium-heavy petroleum oil, and with rubber cements of low and high consistency. It has been shown that the instrument gives values of relative viscosity approximately proportional to absolute viscosities over a range from 7 to 1700 poises.

This automatic viscometer is simple and of rugged construction, having been developed for use as a factory control instrument. It is rapid, time in seconds on the instrument being approximately equivalent to poises. It is well-suited to the measurement of the viscosity of non-conducting liquids, especially when opaque or very viscous.

The practical significance of the measurement of viscosity of rubber solutions is manifold. Although there exists in a general way a proportionality between the quality of a sample of rubber and the inner friction of its solution, the results of test are nevertheless not entirely unambiguous, since the age and previous handling of the rubber are of considerable significance. Also, the presence of light during the measurements causes a decrease in the viscosity.[286] However, the change in viscosity of rubber solutions, after various types of previous handling of the rubber, is often used as a valuable measure of the changes in aggregation, etc. of the rubber. By such means

[284] Compare also with Fr. Kohlrausch, "Lehrbuch der prakt. Physik," 14th Ed., p. 262, B. G. Teubner, Leipzig and Berlin, **1923.**

[285] *India Rubber J.*, **70**, 775 (1925). R. Ditmar in *Chem.-Ztg.*, **49**, 676 (1925) has further described a viscosimeter suitable for practical use with highly viscous liquids. It consists of a glass tube which is closed at the lower end by a wire screen of fine mesh. The time is measured during which a sufficient amount of the liquid runs out to cause a drop in its surface from one marked level to another.

* Translator's note by N. J.

[286] In the light of practical experience, and on the basis of the occasional failure of such physical tests as that of viscosity, it is still necessary to vulcanize experimental compounds, and to test their mechanical properties, if a definite evaluation of the technical quality of a rubber is to be made. Brief mention should be given here of the experiments of LeBlanc and Kröger, who measured, instead of the viscosity of a solution containing sulfur chloride, the time required for gelation of the solution, and used this figure as their measure of quality of the material. [*Kolloid-Z.*, **33**, 168, 348 (1923)]. Compare also with W. Greinert and J. Behre, *Kautschuk*, **2**, 29, 63 (1926).

the effect of high temperature on raw rubber was studied by J. D. Fry and B. D. Porritt.[287] Heating of raw rubber in the presence of air decreases the viscosity of the solution, and in a manner proportional to the temperature used and the length of time the rubber has been heated. However, if the heating is carried out *in vacuo,* with particular care in the exclusion of all traces of oxygen, the heating can be carried to 150° C. without materially affecting the viscosity of the solution made from rubber so treated. It is noteworthy that water vapor, hydrogen, and nitrogen under the same conditions have no effect on the viscosity, while oxygen has a very marked effect, i. e., decreases the viscosity.*

The authors came to the conclusion that the decrease in viscosity of solutions resulting from the milling or masticating[288] of the rubber may be considered equivalent to that brought about by heating the rubber in air. The question is still open, however, as to whether the combined mechanical treatment and heating during milling do not in some special manner cause the disaggregation of rubber. (*See* p. 424.)

A study of the so-called "degradation" of rubber solutions by heat has been made by P. Bary and E. Fleurent† [*Compt. rend.,* **192,** 946 (1931); **193,** 852 (1931); **195,** 665 (1932); **196,** 1796 (1933); *Rubber Chem. Tech.,* **6,** 376 (1933)]. These experimenters find that the decrease in viscosity of solutions of rubber in xylene at concentrations of 1 to 5 per cent, and at temperatures of 44° C. and 92° C. in sealed tubes tends to a limiting value of viscosity which depends on both the concentration and the temperature. One series of experiments, with 5 per cent concentration solutions, was carried out until the viscosity actually reached a constant value for the given temperature. This constancy was reached only after about 10,000 hours of heating. The more dilute the solution and the higher the temperature, the shorter the time required. At this limit the viscosity reaches a final constant value agreeing fairly well with the general formulae of Arrhenius:

$$\log \eta = K c,$$

where η is the ratio of the viscosity of the solution to that of the pure solvent, c the concentration, and K a constant for a given temperature. A better agreement with this equation was found in these experiments at the higher temperature of heat degradation.

Finally there are the viscosity measurements of H. Staudinger and his collaborators, which were planned chiefly to investigate the properties of materials of high molecular weight. In this work, Staudinger was able to draw comparisons by analogy between rubber and polymerization products of other simple compounds whose chemical constitutions were well known. Bearing on this same subject are the experiments of S. Wehrli[289] on the polymerization of styrene, which was found to give different polymers depending on the temperature to which it had been heated and the time it was subjected to that temperature. In a similar manner, experiments were made on polyindene, polyanethole, etc., by M. Brunner,[290] and Staudinger assembled the material into lengthy reports of the extended researches, forming a new division of the knowledge of colloids. He designated those systems in which substances of low molecular constitution (e.g., arsenic trisulfide) are united into colloidal aggregates, as pseudocolloids, and in contrast, he named as eucolloids those substances of such great molecular complexity that no change

[287] *Trans. Inst. Rubber Ind.,* **3,** 203 (1927).

* Translator's Note. The effects of light and heat on the viscosity of rubber solutions have been studied by C. K. Novotny [*Ind. Eng. Chem.,* **26,** 170 (1934)]. The extreme decrease in the viscosity of gasoline cements, and the gelation of carbon tetrachloride cements on exposure to daylight are discussed from the standpoint of photochemical reactions. Practical methods of inhibiting the effects of light and heat are mentioned.—N. J.

[288] Compare also with p. 481 of this book, where the investigations of Klein and Stamberger on the effects of milling are discussed.

† Translator's note by N. J.

[289] Dissertation, No. 439, Zürich, **1926.**

[290] Dissertation, No. 453, Zürich, **1926.** *Cf.* also with the work of E. Geiger, Dissertation No. 422, Zürich, **1926.** Refer also to other publications as noted on p. 454 of this text, footnote 167.

from their colloidal state is possible without the simultaneous change of their fundamental chemical character. To this latter class of materials, which even in their simplest form are still colloidal in nature, belong cellulose, rubber, etc.

Osmotic Properties

The solutions of rubber in the common solvents, such as benzene, benzine, carbon bisulfide, etc., are all of colloidal nature. In consequence of this, the dispersed molecular aggregates are of very high "molecular weight." Frequent determinations have been made of the freezing point lowering of benzene in benzene-rubber solutions, but this effect is so very small that enormous values have been obtained for the molecular weight of rubber.[291] The osmotic method does not permit a distinction to be drawn between a large single molecule built up from an enormous number of atoms, and a micelle, or molecular aggregate whose small individual "building blocks" are held together by the strong van der Waal forces arising from the unsaturated character of the isoprene group of the rubber molecule. Obviously, it is impossible for the solvents mentioned to break any existing bonds. If camphor and menthol are used as solvents, as in the work of R. Pummerer,[292] the freezing point lowering obtained is considerable, and proportionately lower values for the molecular weight of the pure rubber prepared by Pummerer are obtained.

Apparently the last-named solvents, which, in contrast with the usual rubber solvents, are oxygen-containing compounds, cause a loosening of the micelle forces, with the result that the dipole character of the micelle is favored. As a result of this, the number of dispersed particles in this solvent is far greater than that in benzene, thus indicating that the rubber in the benzene solution is in a micellar form. The molecular weights of sol- and gel-rubber, as determined by Pummerer and his collaborators, are of the order of magnitude of from 600 to 1200, and in general are smaller the greater the dilution of the system. Such dependence of the molecular weight on the dilution is not uncommon. In the case of the solution of ethyl alcohol in benzene it is only on extreme dilution that the alcohol breaks down into simple molecular form, while in higher concentrations, the degree of aggregation reaches as high as 6 or 7 molecules per aggregate. It is quite worthy of note that in menthol as well as in camphor, the most soluble rubber fractions, sol- and gel-rubber, show the same average molecular weight, so that in reality, these molecular weights cannot well be doubted.[293] A degree of uncertainty can always be ascribed to the absolute values of such results, and further discussion of them must be limited to the use of their order of magnitude only. Thus values of 10^3 and 5×10^3 are substantially of the same order, as compared with the figure of 10^5 obtained for the micelles of rubber in a benzene solution. After the recent discovery by Pummerer [294] that in the process of freezing

[291] Hinrichsen and Kindscher obtained molecular weights in excess of 3000. According to recent results, however, the purity of the rubber obtained from latex for this work was considered doubtful. Refer also to *Ber.*, **42**, 4329 (1909).

[292] *Ber.*, **60**, 2167 (1927).

[293] Kurt H. Meyer and H. Mark feel that the molecular weights obtained by Pummerer, contrary to their own expectations, are too low. [See *Ber.*, **61**, 1945 (1928)]. The precision of the absolute values determined should be acknowledged or discredited on the basis of experimental work. It is worthy of mention that G. Fromandi, using both pure natural rubber and synthetic rubber, obtained higher values for the molecular weights. But he has admitted that his determinations are less acceptable for their absolute values than for their relative values. See L. Hock, *Z. Elektrochem.*, **34**, 664 (1928) and also G. Fromandi, *Kautschuk*, **4**, 185 (1928). See also Fromandi's detailed Dissertation, Giessen, **1928**, and *Kolloidchem. Beihefte*, **27**, 189 (1928).

[294] *Cf.* lectures delivered by Pummerer and H. Staudinger at the main meeting of the Deutschen Kautschukgesellschaft in Hanover (May, 1929), which are published in *Kautschuk*, **5**, 94, 126, 129 (1929). Pummerer mentioned further the formation of characteristic, fiber-like rubber structures from very cold ether solutions.

benzene from a rubber solution, small bodies of rubber also separate and form a mixed phase with the benzene, it is possible that the molecular weight determinations using menthol require a certain correction, because strong solvation of the rubber might reduce the amount of free solvent to a considerable extent. This correction is at best only a few hundred per cent in magnitude, so that it might not make any appreciable change in the order of magnitude of Pummerer's results.

In contrast with these discoveries, H. Staudinger [295] has stated that in order to determine the molecular weight of materials of such high molecular weight as rubber, all the chemical and physical properties of the substance must be taken into consideration. He also stated that the assumption of much larger molecular aggregates is essential, so the osmotic measurements, which appeared very important in his estimation, still could not be considered as conclusive, especially since it is uncertain whether or not an anomalous action is taking place. It would be advisable to abandon even the investigation of the pure chemical constitution of rubber until a final explanation is found for this serious disagreement in molecular weight determinations. Nevertheless, there are certain physico-chemical considerations which are essential to such an explanation.

Even if the relatively low molecular weights as determined by Pummerer are accepted,[296] it is nevertheless true that the behavior of rubber in the solid state and in the usual solvents makes the existence of large molecular aggregates seem very reasonable. In the close analogy between valence and cohesion which exists particularly in rubber, we see that there is no basic importance to the question as to the origin of the forces which are responsible for the formation of the typical micelles, whether these be of a physical or of a chemical nature. Besides the principal valences which hold together the atoms of the molecule, there are without doubt fields of force which always tend to the formation of larger micelles, whenever no quasi-chemical intervention by the solvent, as in the case of menthol, prevents such formation. From the viewpoint of valence chemistry, the elementary molecules of rubber existing in menthol, for example, must still possess an inherent tendency to recombine into larger bodies or micelles. The apparent reason for the existence of relatively small rubber molecules in such solvents as menthol is that the molecules of the solvent are capable of interacting with the fields of force which surround the rubber molecule because of its unsaturation. This interaction of the solvent with the rubber in no way changes the inherent tendency of the rubber molecules to recombine into larger micelles, on removal of the solvent. Thus the existence of smaller molecules of rubber in such solvents as menthol represents only a temporary condition imposed by the solvent.[297] Actually, rubber which has been dissolved in menthol or in camphor, as soon as it is again dissolved in benzene, gives an indeterminately large molecular weight, showing that it has not been decomposed. It would appear that all opposition to the concept could be removed, if the physico-chemical aspect

[295] See *Kautschuk*, **3**, 237 (1927). These convictions are based on the investigations of Staudinger and his collaborators; *Ber.*, **59**, 3019 (1926); *Z. phys. Chem.*, **126**, 425 (1927), and also *Kautschuk*, **1** (Aug. and Sept., 1925). See also the bibliography on p. 454, footnote 167.

[296] Even if Meyer and Mark are correct in their opinion that the order of magnitude of the molecular weight is 5,000, this value does not seriously affect these considerations, since the micelles, considered to be large molecular aggregates, must always appear of considerable magnitude as compared with the principal valence chains. *Cf.* the following determinations of the osmotic pressure and of the weight of the micelles.

[297] Concerning the theoretical calculations of the intermolecular forces of organic compounds, see Manfred Dunkel, *Z. phys. Chem.*, **A138**, 42 (1928).

were considered in the manner described, and if the existence of small as well as very large molecular aggregates were conceded. This incidentally would simplify the explanation of the fiber structure of stretched rubber. The chemical structural formula to be set up must take into account both cases. At the same time that the relatively small molecular weight in menthol is conceded, it must also be remembered that rubber, even in the pure, free state, tends to exist mainly in the form of micelles even larger than those which are observed in benzene. In the sense of Staudinger, rubber as a eucolloid, when not under the influence of the fields of force of the polar molecules of a solvent, because of its particular chemical constitution, cannot exist by itself in any other form than that of aggregates of extremely high molecular weight, whose existence is not accidental, but is unconditionally essential because of the manner of union of its molecules and atoms. Along with the formation of these "giant molecules," there must be a compatible reversible dissociation process which does not completely destroy the chemical nature of the substance, and which can be caused to take place by the use of polar solvents, such as menthol and camphor.

If the double bonds of rubber are partially saturated by cyclization, as was accomplished by L. Hock and G. Fromandi [298] in progressive steps in the dissolved state by means of the silent discharge, then the viscosity of the rubber solution will become less, in direct proportion to the degree of unsaturation of the rubber. This decrease in viscosity permits the conclusion that the micelles have become smaller. Here again a close relationship between the chemical constitution and the colloidal properties of the rubber becomes evident. This must not be overlooked, and must sometime be explained by the new structural chemistry.

At the inducement of Meyer and Mark, Fikentscher [299] determined the osmotic pressures of rubber dissolved in benzene and chlorbenzene, after similar measurements had been made at the request of Pummerer by Kroepelin,[300] who found micelle weights from 30,000 to 50,000. The direct determination of the osmotic pressure by means of semipermeable membranes was recommended for these high "molecular weights" in preference to the possibly unreliable determination by means of the freezing point lowering. Fikentscher chose for his experiments a membrane of porcelain, which was impermeable to rubber, and measured at 7° C., in the usual way, the height to which the liquid rose in a tube over the membrane. In calculating the molecular weight he considered the solvation of the rubber, because he used the van der Waal modification of the equation of van't Hoff. He found that in solvation, 1 gram of rubber was able to take up 20 to 40 grams of the solvent.[301] The calculated molecular weight was of considerable magnitude. It was found to be largely dependent on the temperature used during the experiment, and on the kind, age and previous handling of the rubber.[302] Therefore, statements of various authors as to molecular weights are not comparable without further information on experimental detail. A crepe rubber (of nitrogen content 0.54 per cent) treated with alkali and dissolved in benzene, gave a molecular weight approximating 160,000, and the same

[298] See the references in the footnote 129, p. 433.

[299] *Ber.*, **61**, 1946 (1928). The first experiments of this type had been performed by W. A. Caspari, *J. Chem. Soc.*, **105**, 2139 (1914). In this work, clay cells were fitted with semipermeable membranes of vulcanized rubber. The average micellar weight was found to be of the order of 1×10^5, as determined in benzene-rubber solutions. See also R. Zsigmondy, *Z. angew. Chem.*, **39**, 401 (1926).

[300] *Kautschuk*, **3**, 233 (1927).

[301] Concerning the solvation power of colloids, see the experiments on gelatins made by J. Eggert and Reitstotter, *Z. phys. Chem.*, **123**, 363 (1926).

[302] *Cf.* the investigations of swelling and aggregation in the previous section, p. 481.

value also in chlorbenzene. An untreated crepe rubber with nitrogen content of 1.05 per cent, gave in benzene a molecular weight of 360,000, but in chlorbenzene, 185,000. The aggregation of the pure rubber prepared by Pummerer from latex could undoubtedly be completely broken down.

At the same time that Meyer and Mark were interested in osmotic experiments, H. Kroepelin [303] again took up their work involving the height to which osmotic pressure caused a liquid to rise. He used the various kinds of pure rubber which were at his disposal in the laboratory of Pummerer. In these experiments, as well as in those of W. Brumshagen, collodion membranes were used after the manner of Bechhold. The calculation of results was carried out on the same basis as that used by Meyer and Mark, even to the point of finding the micelle weight at 11° C. and 40° C., as these authors had done. The order of magnitude of the micelle weight was found to be 2×10^5, being however much greater at 11° C. than at 40° C. On account of the extraordinarily strong solvation of rubber, it is, however, not easy to decide whether the measured pressures are solely osmotic in nature, or whether they are to be considered as swelling pressures. Kroepelin and Brumshagen were able to describe their observations also by means of the equation for swelling pressure as given by Freundlich (*see* p. 475):

$$\log p = a \log c + b$$

In this equation, they found the values at 11° C. to be: $a = 1.7$, and $b = -0.38$; and at 40° C.: $a = 1.8$, and $b = -0.29$. In a similar manner, the results of Duclaux and Wollman,[304] and those of Meyer and Mark, as well as those of Fikentscher, can be represented by straight lines on double logarithmic coordinates, as shown in Figure 98. There is thus some uncertainty as to the interpretation of the experiments on the osmotic rise.[305] Further experiments on rubber in the dissolved state have been made by D. Krüger [306] who showed to what extent the diffusion of dissolved rubber followed the diffusion law of Fick.[307] Through a knowledge of the diffusion coefficient, it is possible, with the aid of an equation developed by Nernst, Einstein and Herzog,[308] to obtain a measure of the size of the molecules of a dissolved substance of high molecular weight. As was to be expected, the results of Krüger show a great scattering. Extremely variable values of the calculated diffusion coefficient result from measurements taken in individual diffusion layers. The meaning of the individual results is thus entirely secondary in importance to the general impression that the rubber exists in micelles of molecular weight of the order of from 10,000 to 100,000. Of the same order of magnitude are the molecular weights as determined by Pummerer on the basis of diffusion experiments with rubber in benzene.

If the great scattering of individual results of diffusion measurements does not permit the determination of any reliable micelle weights, there is nevertheless the possibility of using diffusion methods for the separation of micelles of different size. Obviously, the micelles will never be all of one size, but will exist in a range of sizes. This has been theoretically formulated for a

[303] H. Kroepelin and W. Brumshagen, *Ber.*, **61**, 2441 (1928); Later, H. Kroepelin, *Kolloid-Z.*, **47**, 294 (1929); see also Haller and Trakas, *ibid.*, **47**, 304 (1929).

[304] *Compt. rend.*, **152**, 1580 (1911).

[305] See also the discussion by Pummerer in *Kautschuk*, **5**, 129 (1929). A striking fact mentioned here deserves special attention. "Dead milled" rubber actually shows a decrease in its viscosity, and also a smaller osmotic rise than before milling, in spite of the fact that after "dead milling" an increase in the degree of dispersion must be assumed!

[306] *Gummi-Ztg.*, **42**, 1471 (1928); see also R. O. Herzog and D. Krüger, *Naturwissenschaften*, **14**, 599 (1926).

[307] See Eggert, "Lehrbuch der physik. Chemie," 2nd ed., p. 197.

[308] *Ibid.*, p. 228.

simple colloidal system by M. Volmer.[309] Besides, H. Kroepelin [310] has published a new procedure for diffusion experiments.

The above-mentioned equilibrium, as well as the very closely related solvation equilibrium, is naturally dependent on temperature. (*See* p. 483, Bary's equation.) With slow temperature changes, it suffers readjustment. With sudden "quenching" of heated solutions, an equilibrium [311] may be arrested ("frozen") in a form really corresponding to a higher temperature. R. Pummerer [312] studied these relations by means of viscosity measurements, and found that slow cooling resulted in viscosity of the rubber solutions corresponding to that at the lower temperatures, and that rapid cooling resulted in viscosity of the rubber solutions corresponding to that at higher temperatures. These experiments in particular seem to provide a valuable support for the micelle theory of rubber.

Electrical Properties

It is possible to distinguish, not only voluntary diffusion, but also the movement of dissolved materials under the influence of an electric field. This movement is called electrophoresis. It was first noticed by V. Henri [313] that latex particles in an electric field migrate towards the anode, and may thus be considered as carrying a negative electric charge. From these observations, T. Cockerill,[314] followed by Sheppard and Eberlin,[315] developed a process for the electrodeposition of rubber from latex or from water emulsions. In this process, if negatively charged pigments are suspended in the liquid, a complete rubber compound may be deposited at one operation. With the further technical development of the process, which as such will be mentioned only briefly here, further work was carried out on the scientific aspect by S. E. Sheppard.[316] He found that the latex particles carried a negative potential of 35 millivolts, and possessed a migration velocity of 2.7×10^{-4} cm. per sec. per volt per cm. Their electrophoretic velocity is thus quite similar to that of many other materials which exhibit this property.

In benzene solution, however, no apparent electric charge was found by R. H. Humphry and R. S. Jane.[317] In order to observe electrophoretic migration in these colorless sols, they used the "streak method" (Schlierenmethode) of A. Toepler.* The use of this method for this purpose had been proposed earlier in an incidental manner by L. Hock.[318] In case the sols are not perfectly dry, the rubber particles may assume either positive or negative charges.

By precipitation of synthetic rubber which had been produced by silent electric discharge in decalin solution, G. Fromandi [319] obtained a quite stable, milky emulsion on the addition of acetone. In this material, particles were

[309] *Z. phys. Chem.*, **125**, 151 (1927).

[310] *Kolloid-Z.*, **47**, 294 (1929).

[311] Concerning this subject in general, see the above text by Eggert, pp. 253 and 442.

[312] *Kautschuk*, **5**, 129 (1929).

[313] *Compt. rend.*, **144**, 431 (1907).

[314] See Clignett, "Rubber Recueil," p. 377, J. H. de Bussy, Amsterdam, **1914**. Also T. Cockerill, *India Rubber J.*, **37**, 331 (1909); Brit. Pat., 21,441 (Oct. 10, 1908) and Ger. Pat., 218,927 (Oct. 11, 1908).

[315] *India Rubber J.*, **70**, 21 (1925); and Sheppard, *India Rubber World*, **73**, 193 (1926); *Rubber Age (N. Y.)*, **21**, 76 (1927); *Nature*, **119**, 129, 393 (1927).

[316] *Trans. Am. Electrochem. Soc.*, **52**, 47 (1927).

[317] *Kolloid-Z.*, **41**, 293 (1927).

* Translator's Note. The German edition refers to Fr. Kohlrausch, "Lehrbuch der praktischen Physik," 14th ed., p. 310, B. G. Teubner, Leipzig and Berlin, **1923**. The translator submits as a supplementary reference describing a similar experimental technique: C. Camichel and P. Dupin, *J. Rheol.*, **3**, 415, 420, 422, 427 (1932). — N. J.

[318] *Kolloid-Z.*, **37**, 365 (1925). A note in discussion of a paper by Kruyt, *ibid.*, **37**, 358 (1925).

[319] Dissertation, Giessen, **1928**. This work appeared also in *Kolloidchem. Beihefte*, **27**, 189 (1928).

seen under the microscope to be in lively Brownian motion. Under the influence of an electric field, these particles showed their negative charge by migrating to the anode.

Optical Properties (Absorption Spectrum)

As would be expected from the absence of color of rubber sols, there are no absorption bands in the visible region. It was first determined by S. J. Lewis and B. D. Porritt [320] that no absorption bands existed at wave lengths greater than 270 mμ, in the case of pure rubber. An extensive study of the spectral behavior of completely purified rubber in the ultra-violet region was made by G. Scheibe and R. Pummerer.[321] This work, on the one hand, should indicate whether it is possible to control the purification of rubber by optical means, and whether the separate fractions can be identified by similar means; and on the other hand, should provide a basis for the explanation of the chemical constitution of the rubber hydrocarbon. The present discussion will be restricted to the statement of the experimental facts, which will be used elsewhere in the text.

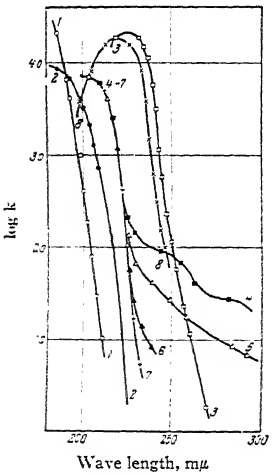


Figure 100—Absorption spectra of various rubber preparations (along with those of some similar materials).

(According to G. Scheibe and R. Pummerer.)

1. Diallyl.
2. Trimethylethylene.
3. Dimethylbutadiene.
4. Latex, purified with NaOH, by fractional precipitation.
5. Latex, uncoagulated.
6. Latex, purified with NaOH.
7. Sol rubber.
8. Isoprene.

The solvent used, hexahydrotoluene, distinguished itself by good optical transmission into the far ultra-violet. The solution of the various rubber samples was carried out with careful exclusion of air, using an atmosphere of carbon dioxide. The concentration of the solutions was expressed in terms of mols of isoprene per liter, since the actual molecular weight of rubber was unknown. From the measurements it was possible to calculate the molecular absorption coefficient k [322] whose common logarithm is used as the ordinate in Figure 100. The abscissa of this graph is the corresponding wave-length in millimicrons (mμ).

[320] *J. Soc. Chem. Ind.*, **40**, 18T (1921).

[321] *Ber.*, **60**, 2163 (1927). See also Pummerer und Koch, p. 237 of this text.

[322] The definition of the molecular absorption coefficient is as follows: k denotes the reciprocal thickness of that layer of material, in cm., which, in a concentration of 1 mol/l., must be used to weaken the intensity of the light passing through the layer to 1/10 of its incident intensity. See also F. Weigert, "Optische Methoden der Chemie," Akad. Verlags-Ges., Leipzig, **1928**. In this book are treated both the theoretical and practical aspects of this type of measurement. See also the text by Eggert, p. 475.

Curves 4 to 7 are for rubber preparations; the others for materials which may well be compared with rubber with respect to their optical behavior. From the graphs for rubber of different degrees of purification, the conclusion may be drawn that the steep part of the curves above log $k = 2$ follows the same course for all sorts of rubber. It is thus possible to identify curve 7, taken for sol rubber, with pure rubber itself. The graph indicates that appreciable absorption occurs only below 240 mμ, and that the maximum absorption exists at about 200 mμ. It is worthy of note that purified gutta-percha, also dissolved in hexahydrotoluene, showed complete agreement with the absorption curve of pure rubber, a fact which indicates that the number and type of double bonds in both cases must be very similar. The effect of the double bond on the absorption curves of comparable compounds is shown in curves 1 (diallyl; two double bonds separated by carbon atoms), 2 (trimethylethylene; one ethylene group), 3 (dimethylbutadiene; conjugated double bonds) and 8 (isoprene, which differs from the last named methylisoprene [dimethylbutadiene] only by a slight shift of its absorption curve towards the ultra-violet).

There are no measurements of the dependence of the absorption spectrum of rubber solutions on the nature of the solvent. Such measurements would doubtless prove interesting and useful in further clarifying the matter of molecular weight, which was discussed on page 490. This would be particularly true if the choice of solvents included those with large dipole moments, such as menthol, octyl alcohol, etc., which penetrate rubber very thoroughly. In hexahydrotoluene, which must possess only an insignificantly small dipole moment, rubber becomes dissolved without doubt in a micellar manner, much the same as it does in benzene, which has no dipole moment. Thus the absorption spectra given will apply equally well to rubber dissolved in benzene. With the use of menthol, etc., one would expect to find different results.

Rubber as a Dispersing Medium for Solid Substances (Theory of Filler Reinforcement)

Experimental Facts

Experience has shown that the addition of the so-called "active fillers" to rubber improves its mechanical properties. The effect is especially striking in the case of certain kinds of gas black, of zinc oxide, clay, basic magnesium carbonate, and other additives. The work required to rupture such a mixture, when calculated to the same rubber content, is very much greater than that required for a filler-free vulcanizate. It has been found that this "strengthening" action of active fillers constitutes a specific property of each such substance and in general is the greater, the finer the state of subdivision.

Although the art of compounding technical rubber mixtures is specifically concerned with the selection of the ingredients, with respect to both kind and amount, for obtaining a product of the desired properties, correlated and generally accessible facts concerning the influence of the different fillers on the properties of the vulcanizate are still lacking. Insofar as the results of the earlier investigators in this field have been published, they lack so much in theoretical foundation and treatment that no deep insight into the mechanism of filler action can be obtained from them.

Nevertheless, the older investigations unquestionably have historical significance, for, in addition to transmitting the empirical art of compounding,

they constituted the first attempts to develop a system that would establish the influence of each compounding ingredient, both in kind and amount, on the mechanical, chemical, electrical, and other technically important properties of vulcanized mixes. This goal has not yet been reached, even today, and, in spite of some very fine and important partial results, actual experience still plays the essential part in the practical work of the rubber technologists. Unmistakable, however, is the influence which the scientific method of attack on these problems has had upon the continuous increase and enrichment in the quality of the experimental results. If they had been guarded carefully as an art and carried forward as a professional tradition, they would not have been the source of such significant and far-reaching developments as have been observed in the last ten years, thanks to the growing recognition of the value of scientific research and the profitableness of a well-equipped laboratory.

In this summary, the physical and physico-chemical aspects will be emphasized. Questions of compounding, which are so important in rubber technology, will therefore be alluded to only insofar as they have theoretical significance from a physical standpoint. Nevertheless, since it is proposed to delve deeply into the theory of filler action, reference in a very general way to the most important and useful rubber fillers should not be omitted.

The common conception that fillers are solely diluents and, economically considered, are cheapeners for rubber, is entirely wrong, though in certain cases and for good reasons they must fulfill these functions. Quite often the price of a filler, which cannot be left out of a compound for definite reasons, is higher than that of the rubber itself. Besides, it does not necessarily follow that the dilution of rubber with fillers always results in a deterioration of its valuable properties. On the contrary, those fillers which are most important technically may give to the mixture properties which often surpass those of the corresponding pure-gum mix, properties which cannot be developed from rubber alone. Aside from these generalities, there is in every case some definite requirement placed upon the mixture. This may be one of color, of stability towards chemical reagents, of electrical insulating properties, of the greatest possible or again, of the least possible, extensibility. It may consist in the degree of the elastic after-effect, in the abrasion resistance, in the strength, hardness, or compactness, or again, in the stability on storage or behavior under conditions of low temperature or intense heat. In short, there are a thousand requirements which are prescribed by the application of the product. Usually several of these requirements must be met in a single mixture. The art of the compounder, however, consists not only in fulfilling these technical conditions, but also in complying with the economic requirements, a task which is of very great importance. In fact it is often much easier to make a remarkable product, if it may be an expensive one, than a cheap one on which considerable demands are made. However, the composition and nature of a mixture are determined not only by the properties required in the finished product, but also, often to a limiting degree (and sometimes in a sense directly opposed to the ultimate object), by the conditions imposed by the method of fabrication. It may perhaps be imperative that a mixture in the raw condition be characterized by high tackiness, or that it shall have the minimum tackiness, or that it be sufficiently plastic to be tubed, or that it be sufficiently rigid in the raw condition not to collapse, or that it shall comply with whatever other limitations the manufacture of the

intermediate steps places upon the properties of the mixture.* When it is considered that the number of commercially applicable fillers is not small, and that in most cases they are not employed separately, but jointly with several others, in which case they do not always behave in an additive manner,** then the immense number of possibilities, as well as the extent of the difficulties which limit the compounding, are evident. Today more than ever before the effective performance of a product is the first technical requirement, and intuition, experience, and unflagging perseverance in investigation still remain the most important qualifications for the chemist in handling the difficult and responsible task of developing the compound.

The following enumeration of the more important fillers is not the place in which to discuss their often highly diversified effects; a survey which points out the existence of certain typical groups of fillers is sufficient.

Aside from the case of cold vulcanization, sulfur is almost always the indispensable constituent of the mix, since it is of first importance in the vulcanizing process.

If the compound must have exceptional "nerve" and have the property of absorbing a large amount of energy, it requires the addition of one of the so-called "active" fillers. Among these active fillers carbon black stands at the head of the list.† There are many kinds of carbon black, differing widely in both physical and chemical properties. Reference is made especially to the oil blacks and, besides these, to the American gas blacks, which are obtained from natural gas by incomplete combustion or—in the case of the so-called thermal decomposition blacks—by pyrogenetic decomposition. As a rule the activity of a given filler increases with increasing degree of dispersibility or dispersiveness‡; in this, the particle size is not alone the determining factor; of greater importance are the specific surface relations. This will be discussed in greater detail later.

Besides carbon black, zinc oxide, which appears on the market in several degrees of fineness, is an outstanding active filler, as are also basic magnesium carbonate and certain clays. Zinc oxide has further significance in being an activator for organic accelerators. On the other hand, there are the cheap compounding ingredients, which act chiefly as diluents. Chalk and barytes belong to this class of materials, as does also infusorial earth, which, like barytes, finds application in acid-resistant mixes.§ An artificially prepared colloidal silica, which may also behave as an active filler on account of its fineness, also serves this same purpose, that is, imparts acid resistance.

* Translator's Note. In this connection the recent work of W. F. Busse and J. M. Davies, presented at the Chicago meeting of the Rubber Division of the American Chemical Society (September, 1933), is of interest. These investigators have shown that a masterbatch of rubber and carbon black slowly increases in stiffness on standing at ordinary temperature, and more rapidly when the masterbatch is heated subsequent to the milling operation. — N. A. S.

** Translator's Note. As far as the translator is aware, no satisfactory proof that the blending of pigments produces more than purely additive results has been published.—N. A. S.

† Translator's Note. For an extensive review and bibliography on the use of carbon black in rubber, see N. A. Shepard, "Carbon Black in the Rubber Industry" (in J. A. Alexander, "Colloid Chemistry," Vol. IV, p. 309-350, Chemical Catalog Co., Inc., New York, 1932). — N. A. S.

‡ Translator's Note. It is believed that this is an accurate translation but an inaccurate statement. In the translator's opinion the correct statement would be: "The greater the difficulty in dispersing a given pigment, the greater, as a rule, is its activity." Perhaps what the author had in mind was that the *reinforcement* of the rubber-mixture increases with the increasing degree of dispersion of the active filler. — N. A. S.

§ Translator's Note. Recently a comprehensive comparison of the reinforcing value of powders for rubber has been published by A. A. Somerville [*Vanderbilt News*, **3**, No. 3 (1933)]. Using tensile strength as the measure of reinforcement, the samples of channel black, magnesium carbonate, zinc oxide, clay and treated whiting were definitely reinforcing in effect; blanc fixe and titanium dioxide showed slight reinforcement; and lithopone and a sample of thermal decomposition black were neutral in effect (23-volume loading). Ordinary whiting and talc acted solely as fillers. — N. A. S.

Besides the organic accelerators, which are used only in low concentration, the inorganic accelerators, among which litharge and magnesia are the most important, have been used for a long time.

The color of the mixture is influenced by the addition of pigments. The blacks, mentioned above, are used for producing gray, bluish and black colors. Litharge may be applied for a similar purpose, since it reacts with the sulfur to form the black lead sulfide.

Lithopone, which is a mixture of zinc sulfide and barium sulfate formed by simultaneous precipitation, as well as zinc oxide and especially titanium oxide, all have remarkable covering power. These white pigments, because of their high indices of refraction, are only slightly masked by the rubber and therefore have, according to Twiss,[323] especial covering power, while whiting, magnesium carbonate, alumina, and some other substances have refractive indices only slightly different from that of rubber, and therefore only slight covering power. For a given pigment, covering power increases with decreasing particle size. Extremely small particle size accounts, in large measure, for the blackness of the carbon blacks.[324]

The antimony sulfides produce red colors. Usually they contain more or less free sulfur in addition to the trisulfide [325] or a mixture of the tri- and pentasulfides. To a lesser extent, red or brown colors are obtained with ferric oxide.* Mercury sulfide is a very valuable red pigment of special brilliance.

Green, yellow, and other colored rubber mixes are also made for special purposes. These colors are often obtained by the addition of organic dyestuffs which are stable under the conditions of vulcanization, but there are also available the important mineral pigments, the green chromium oxide, the yellow cadmium sulfide, and the blue ultramarine.

Factice in its different forms is also of importance as a compounding ingredient for rubber. Brown factice, in the form of elastic blocks which crumble under pressure, is obtained by the action of sulfur on the hot glycerides of unsaturated fatty acids, especially rapeseed oil; white factice is formed by the reaction of sulfur monochloride [326] on the cold oil, in a manner similar to the cold vulcanization of rubber. Pastes consisting of colloidal dispersions [327] of factice in water, which make factice suitable for mixing directly with latex, have recently also found application. Besides its importance as an elastic filler, factice has a retarding effect on vulcanization. At the same time, it acts as a so-called "softener," plasticizing the uncured stock.

Finally, reclaimed rubber, prepared by one of the many mechanical or chemical processes, is an important compounding ingredient which should be classified along with factice and other fillers, in that it also forms only a heterogeneous mixture with the rubber. The rubber hydrocarbon contained in these regenerated rubbers—which never lose certain of the properties of a vulcanizate—does not blend with the new rubber to form an homogeneous mixture.[328]

Materials designated as softeners are used in mixes prepared from tough plantation rubbers, in order to improve the processing on the mills, in the

[323] *India Rubber J.*, **65**, 607, 651, 693 (1923).

[324] *Cf.* L. Hock, *Kautschuk*, **4**, 266 (1928); F. Hebler, *Kolloid-Z.*, **41**, 365 (1927); and F. V. v. Hahn, "Dispersoid Analysis," p. 123, Steinkopff, Dresden, **1928**.

[325] *Cf.* also L. Hock, *Kautschuk*, **1**, 11 (Dec., 1925).

* Translator's Note. In America red oxides have largely replaced the antimony sulfides in the manufacture of red articles. — N. A. S.

[326] For a factice-like product obtained by electrical discharge, "Voltol Factice," *see* L. Hock, *Kautschuk*, **2**, 65 (1926); also C. L. Nottebohm, Dissertation, Giessen, **1929**, and L. Hock and C. L. Nottebohm, *Kolloidchem. Beihefte*, **31**, 185 (1930). *See also* B. C. J. G. Knight and P. Stamberger, *J. Chem. Soc.*, p. 2791 (1928).

[327] The particles, suspended in a large amount of water, exhibit Brownian motion.

[328] See page 429, footnote 120.

tubing machines, etc. Their action consists in an influence on the interfacial forces at the surfaces of the rubber and the pigments.* Among these softeners are bituminous substances (asphalts), which in general are incorporated in very considerable quantities in the mixtures and which themselves undergo a sort of vulcanization; also, other materials, which even in small amounts have the desired effect, as for example, certain glycerides, higher fatty acids (stearic acid), mineral oils, paraffin, vaseline, rosin, tar, rubber resins, rosin oil, and other naturally occurring substances or preparations.

In order to suppress the deterioration of rubber mixes on aging, brought about by oxidation, the so-called "antioxidants" are added; for example, nitrogen-containing bases of the aromatic series,[329] paraffin and certain special preparations. Many of the materials mentioned as softeners fulfill this purpose.

Since the success of a mixture is dependent in high degree on the number and kind of fillers used, the selection and testing of them is of special significance. Often the physical aspects (particle size, etc.) play a more important part than the chemical characteristics. As a result, the study of the fillers has special significance, as has been emphatically pointed out.[330] It is impossible, however, to give more space here to this closely related subject. Special attention has to be given to the careful mixing of the pigment in the rubber and to its uniform distribution in this medium, as well as to the state of the pigment itself. There exists in this field an extensive and valuable literature which can only be briefly mentioned, since our attention in this connection must be given only to the general physical features and not to the technical details, however important they may be.[331]

While in the earlier days the application of fillers was dealt with only from a purely empirical point of view, C. Heinzerling and W. Pahl [332] undertook to determine the influence of a certain additive on the mechanical, chemical, and electrical properties, as well as on the thermal behavior of the vulcanizate. These first and therefore fundamentally very important investigations did not produce general rules and extensive results, but they induced studies in this field by others, which led to a continuously improving system of experimenting. Thus, through the impetus of these pioneers who first recognized the significance of studies on fillers, there followed the extensive investigations of Ditmar,[333] of P. Breuil [334] and others.[335] Investigations of this kind

* Translator's Note. This is a very broad statement, giving only one phase of the action of softeners. It is well known that softeners have a definite softening action on the rubber itself, increasing its plasticity and hence workability. See W. N. Burbridge, *Inst. Rubber Ind. Trans.*, **1**, 429 (1926); also E. C. Zimmerman and L. V. Cooper, *Ind. Eng. Chem.*, **20**, 812-3 (1928). — N. A. S.

[329] First mentioned by Wo. and Wa. Ostwald (1908). *Cf.* the lecture by Wo. Ostwald, cited on p. 417 of this book.

[330] Compare the above-mentioned work of F. V. v. Hahn on "Dispersoid Analysis," the work of Wiegand (in the following section, p. 500), as well as that of L. Hock and S. Bostroem, *Kautschuk*, **3**, 21 (1927) and F. Evers, "Sedimentation Analysis of Fillers," *Kautschuk*, **3**, 70 (1927), and especially, LeBlanc, Kröger and Kloz, *Kolloidchem. Beihefte*, **20**, 356 (1925); also H. Green, *J. Franklin Inst.*, **192**, 637 (1921) ("Microscopic Estimation of Particle Size").

[331] See, for example, St. Reiner on the "Homogeneity of Mixtures made by the Masticating and Mixing Processes," *Kautschuk*, **1**, 9 (Nov., 1925); further, on the "Irregularity of Filler Distribution," *Gummi-Ztg.*, **42**, 1359 (1928); as well as H. Page, *Inst. Rubber Ind. Trans.*, **4**, 521 (1929). For the recognition and distribution of fillers in the finished mixture, and the detection of mixing errors, see the article of F. Kirchhof on the "Use of the Quartz-Mercury Lamp," *Kautschuk*, **4**, 24 (1928); also P. G. Nagle, *Inst. Rubber Ind. Trans.*, **3**, 304 (1928); also *Gummi-Ztg.*, **42**, 1745 (1928). Recent work with filtered ultra-violet light is discussed on p. 642 of this book.

[332] *Verhandl. d. Vereins Beford. d. Gewerbefl.*, 415 (1891); 25 (1892); *J. Soc. Chem. Ind.*, **11**, 536 (1892).

[333] *Gummi-Ztg.*, **20**, 394, 733, 844, 1077 (1906); **21**, 103, 234, 418 (1906-7).

[334] *Caoutchouc & gutta-percha*, **1**, 76 (1904).

[335] For example, Beadle and Stevens, *J. Soc. Chem. Ind.*, **30**, 1421 (1911); H. W. Greider, *J. Ind. Eng. Chem.*, **14**, 385 (1922) and *India Rubber J.*, **64**, 845 (1922); H. F. Schippel, *J. Ind. Eng. Chem.*, **12**, 33 (1920); *cf.* p. 415 of this book.

proved really productive from a scientific as well as a technical standpoint only when a fruitful hypothesis, which could give the guiding principle, was found. To such hypotheses, the discussion will now be directed.

Influence of Fillers on Work Capacity

When Twiss [336] emphatically pointed out that the strength and toughness of a rubber mix increased with increasing fineness of the mineral filler added, a fruitful foundation was laid for the further study of filler problems.

At about the same time, W. B. Wiegand [337] rendered the extraordinary service of showing, through suitably conceived and carefully thought out experiments, that a close relationship exists between the surface of a filler and its reinforcing effect, and that this is attributable to the surface forces between the filler and the rubber, which wets it. In his work with different fillers, he showed that their reinforcing power depended upon the concentration. It was of great significance to the effective evaluation of his measurements that Wiegand did not confine himself only to determining and comparing the tensile strengths and elongations of the various mixes in the usual way, but that he also made the comparison with the aid of an energy "measuring stick," by using both data to calculate the "work of tearing or breaking." In other words, he determined the maximum capacity of the different mixtures for storing up energy. If the stress-strain curve in the rupturing test is plotted in a co-ordinate system (ordinate: stress; abscissa: elongation), the area enclosed by the curve and the abscissa can be determined by means of a planimeter and expressed in terms of energy, as for example in kg. m. or in calories.

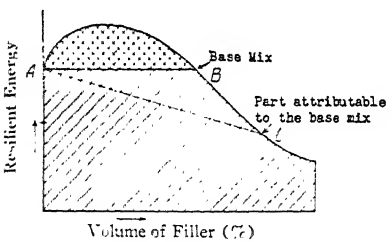


Figure 101—Dependence of the resilient energy (in kg. m./cc.) of vulcanized rubber on the filler content (in volume per cent, based on the volume of raw rubber used).
(According to W. B. Wiegand.)

(AB = resilient energy of the base mix; AC = that portion of the resilient energy due to the base mix. Double lined area = "ΔA — function."

This then can be calculated to a cubic centimeter of the unstretched compound.[338] Wiegand designates this work of rupture (expressed by him in foot-pounds per cubic inch—English system—in which a ft. lb./cu. in. corresponds to 0.00844 kg. m./cc. or 0.0198 gram cal./cc.) as "proof resilience."[339]*

[336] Society of Chemical Industry. Reports of the Progress of Applied Chemistry, **4**, 324 (1919).
[337] *India Rubber J.*, **60**, 379, 423 (1920); further, especially, *Inst. Rubber Ind. Trans.*, **1**, 141 (1925).
[338] *Cf.* p. 405 of this book.
[339] For calculation:

1 ft. =	0.3048 m.
1 lb. =	0.4536 kg.
1 cu. in. =	16.387 cc.
1 ft. lb. =	0.3048x0.4536 = 0.13826 kg. m.
1 ft. lb./cu. in. =	0.13826 ÷ 16.387 = 0.008437 kg. m./cc.
1 kg. m./cc. =	118.53 ft. lbs./cu. in.
1 kg. m. =	2.342 g. cal.
1 ft. lb./cu. in. =	0.0198 g. cal./cc.

These equivalents are used in Table 14.

* Translator's Note. For information on the energy or work of retraction as compared with energy of extension, *see* F. S. Conover [*Ind. Eng. Chem.*, **22**, 871 (1930)] and H. Barron and F. H. Cotton [*Inst. Rubber Ind. Trans.*, **7**, 209 (1931)]. Conover concluded that the work of retraction for any given elongation is practically independent of either the kind or amount of powder used. The latter investigators obtained figures quite contrary to those of Conover. The work of retraction increased progressively with increase in volume of pigment up to a maximum in the case of reinforcing materials and varied directly with the work of extension. However, the increases in energy of retraction were of a relatively low order. — N. A. S.

In order to determine the influence of increasing amounts of a filler on the proof resilience of a mix, Wiegand chose as his base mix one which consisted essentially of rubber and the required curing ingredients. It was so selected with respect to vulcanizing characteristics that the work of rupture at the given temperature of vulcanization was in large measure independent both of the vulcanization time and of the widely differing effects of the different fillers on the vulcanizing properties. This base mix consisted of 100 volumes of rubber, 3 volumes of litharge, and 2.5 volumes of sulfur, which correspond to 100, 30, and 5 parts by weight, respectively. Vulcanized for from 15 to 45 minutes, at 141° C., it gave vulcanizates of approximately the same proof resilience at each cure.[340] By mixing the series in which 10, 20, 30, etc.[341] volumes of filler to 100 volumes of the rubber are added, and by taking the tensile strengths of the separate mixtures, a curve may be constructed which shows these values in relation to the concentration of filler. Figure 101 shows in a zinc oxide mix, for example, how with increasing amounts of the filler, the proof resilience at first becomes greater than that of the base mix, reaches a maximum, and then at higher concentrations again drops. In Figure 102 the individual stress-strain curves are shown in a spatial model. If the strength of the base mix is represented by the horizontal line *AB* in Figure 101, then the area enclosed by it and the curve, which is obviously a measure of the reinforcement inherent in the filler, is the "ΔA-function," according to Wiegand.

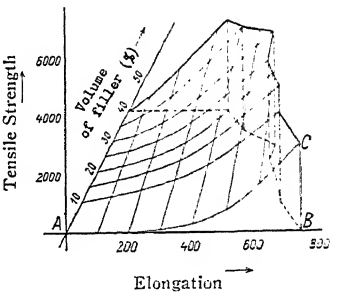


Figure 102—Spatial model of the stress-strain curves for vulcanizates with increasing filler content.
(According to W. B. Wiegand.)

ABC = area corresponding to the proof resilience of the base mix with 0 per cent filler.

[340] D. F. Twiss and F. B. Jones have made special mention of the peculiar behavior of mixtures like the above, which give optimum mechanical properties over a very broad range of cure ("plateau-effect"). The tensile curve, independent of the time, exhibits a very broad maximum. See *J. Soc. Chem. Ind.*, **42**, 505 T (1923).

[341] The following illustrates the calculations: In 105.5 volumes of this base mix there are 100 volumes of rubber, i. e., 94.8 vol.-%. If the ingredients measured in vol.-% are referred to the vol. of rubber in the final mix, and the same is reduced to 100, then, for example, there is obtained for a 20 vol.-% filler addition, a final mix which contains 20 cc. of filler, and 100 cc. of rubber in 125.5 cc. of the mix. The rubber content is 79.7 per cent by volume. The rubber content of the final mixture is only 84 per cent of that of the base mix. Eighty-four hundredths of a cc. of the control is thus identical in its rubber content with 1 cc. of the final mix. This relation was used in the calculation of column 6 in Table 14.

In calculating weight percentage over to volume percentage, the following formulas may be used:

$$(1)\ f = \frac{100\,F}{100k - F(k-1)}; \qquad (2)\ F = \frac{100\,k}{\frac{100}{f} + (k-1)}$$

f = vol.-% filler
F = wt.-% filler
$k = \frac{S_f}{S_k}$, with S_f the specific gravity of the filler and S_k the specific gravity of the medium, in this case, of the rubber.

In using this equation, f is the vol.-% of filler, when the total volume of the mixture is 100; F the wt.-%, provided the total weight of the mixture is 100. [See also the dissertation of F. Hartner, Giessen (1929); *Kolloid-chem. Beihefte*, **30**, 83 (1929); *Rubber Chem. Tech.*, **3**, 215 (1930)].

: to the author not to make the horizontal line ...ne reinforcement, but rather the oblique line AC, in which the reinforcement is referred to the amount of rubber contained in the mixture of that particular concentration, the amount decreasing with increasing filler content. In that case the area enclosed by the curve above the straight line AC would be designated as the ΔA-function (*cf.* column 6 in Table 14).

TABLE 14.—*Activity of Various Fillers (W. B. Wiegand).*

1 Nature of mix (II - IX contain 20 Vol.—% of Filler)	2 Work capacity (proof resilience) Ft.lbs. /cu. in.	3 Kg.m. /cc.	4 gram cal. /cc.	5 Difference between the proof resilience of the mixture containing filler and the base mix (per cent)	6 Increase in proof resilience calculated on the same rubber content; i.e., on 84% of the base mix (per cent)	7 Surface area of the filler (sq. in. /cu. in.)
I Base Mix	450	3.80	8.89	—	—	—
II " " + gas black	640	5.40	12.65	+ 42	+ 69	190.5×10^4
III " " + lampblack	480	4.05	9.48	+ 6.6	+ 27	152.4×10^4
IV " " + clay	405	3.42	8.00	— 10	+ 7	30.5×10^4
V " " + ferric oxide	355	3.00	7.01	— 21	+ 1	15.2×10^4
VI " " + zinc oxide	530	4.47	10.47	+ 18	+ 40	15.2×10^4
VII " " + chalk	410	3.46	8.10	— 9	+ 8	6.1×10^4
VIII " " + infusorial earth	365	3.08	7.21	— 19	— 3	5.1×10^4
IX " " + barytes	360	3.04	7.11	— 20	— 4	3.0×10^4

In comparing the different fillers with respect to their reinforcing effects, the amounts of filler are laid out along the axis of abscissae, always in volume percentage and not by weight, as the latter is obviously without significance in this interfacial system. Incidentally, Wiegand's methodical procedure for presenting the facts in a rational manner is distinctive and quite ideal. Figure 103, I to VI, presents the characteristic curves for a number of important fillers. Obviously it is important for the technologist not only to know with which filler the maximum work capacity can be obtained, but also to observe from the curve itself whether the reinforcing effect persists over a broad range of concentrations, or whether after reaching an optimum loading, a very sharp decline in work capacity occurs, making it dangerous to exceed this concentration. In all cases, with increasing filler content, deterioration of the mix finally takes place, as the result of progressively less perfect blending of the rubber and filler.[342] The facts presented in Fig. 103, I to VI, may well be supplemented by several numerical values, which are taken from the work of Wiegand [343] and recalculated into the metric system. In Table 14, column 1, the fillers investigated are listed. In the second, third, and fourth columns, the proof resilience values of the mixtures with a 20 volume-per cent loading are given. These values are calculated in (1) ft. lbs./cu. in., (2) kg. m./cc., and (3) gram cal./cc. In column 5 figures are given which show in per cent the extent to which the proof resilience figures of the mixtures containing filler are greater than that of the base mix, which had

[342] *Cf.* also F. Hartner, Dissertation, Giessen, 1929; *Kolloidchem. Beihefte*, **30**, 83 (1929); *Rubber Chem. Tech.*, **3**, 215 (1930).

[343] The graphs 101 to 103, with the introduction of the straight line AC, are taken from the publication of W. B. Wiegand in *Ind. Eng. Chem.*, **17**, 939 (1925). For the calculations, see the footnote on page 500.

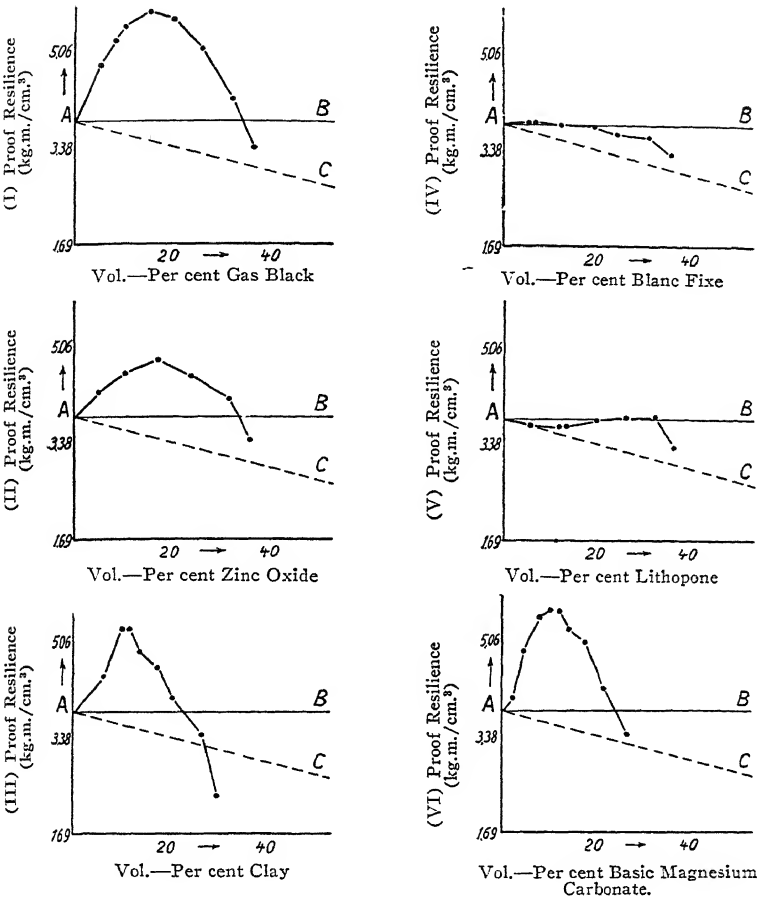


Figure 103—Dependence of the proof resilience (in kg. m./cc.) of vulcanized rubber on the content of filler (in volume per cent, based on the volume of raw rubber used.) (According to Wiegand and Greider.)

AB = proof resilience of the base mix.

AC = that portion of the proof resilience attributable to the base mix.

a value of 3.80 kg. m./cc., i. e., the amount above the horizontal line AB (Fig. 101). In column 6 the same calculation is made but, in this case, referred to the actual amount of rubber contained in the mix, and corresponding to the points on the straight line AC.[344] Finally, in the last column, there are given the surface areas in sq. in./cu. in. of filler, according to Wiegand, as they were ascertained by microscopic measurement, based upon particle size. It seems clear that there is an unquestionable relationship between the reinforcing action of a filler and its surface area.

[44] The rubber content of the several mixes is only 84 per cent of that of the base mix. Therefore, the work of rupture of the mixes containing filler is to be compared with 0.84 of the work capacity of the base mix, thus 0.84x3.80 = 3.19 kg. m. Thus the gas black mixture, with a work capacity of 5.40 kg. m., surpasses the base mix to the extent of approximately 69 per cent when calculated on the basis of the *same* rubber content.

With certain changes in method, but fundamentally in a similar manner, other observers, especially North [345] and Greider [346] later duplicated the measurements of Wiegand and corroborated them remarkably well. These investigations have been much discussed from a technical standpoint in the scientific literature.[347]

The reinforcing action of fillers naturally depends not only on their kind, particle size,* and the intimateness of the mixing,[348] but also on the nature of the rubber [349] used. The other materials used with them are also of significance. The particle shape is likewise of importance.† H. A. Depew has made some observations on the mechanism of reinforcement, which are based on the hypothesis that in the case of active fillers the adhesion between the filler and the rubber particles is even stronger than that between the rubber particles themselves. The deliberations of J. T. Blake [350] are along this same line.‡ He discusses in a very interesting way the role of the natural and artificial dispersing agents for pigments, as, for example, of stearic acid for carbon black, from the viewpoint of their polarity, and as Wiegand [351] did earlier, made observations on the maximum amount of filler that could be dispersed.§ With the growing importance of the direct incorporation of fillers in latex,[352] the study of this type of mixing is becoming more and more interesting. It can be predicted in this case that in eliminating the rupturing of the latex particle by mastication, the mechanism of reinforcement will have to be considered from an entirely new viewpoint. It is hoped that the problems connected with active fillers will be attacked from all angles so that a clearer insight and more definite control will be obtained. The investigations, such as those of LeBlanc [353] and his collaborators and of

[345] *India Rubber World*, **63**, 98 (1920).

[346] *J. Ind. Eng. Chem.*, **14**, 385 (1922).

[347] F. Kirchhof has extended these investigations to colloidal silica. See *Gummi-Ztg.*, **39**, 2102 (1925).

* Translator's Note. G. S. Haslam [*Rubber Chem. Tech.*, **6**, 288 (1933)] has attempted to show the relationship between the influence of particle size and of surface area. While his results are not conclusive, they indicated that in the case of the zinc oxide samples with which he was working, the tensile strength was more closely related to the surface of the pigment than to the particle size. — N. A. S.

[348] See the conference report in the *India Rubber J.*, **72**, 227 (1926) containing the contributions of several technologists on the influence of the characteristics of the particle: P. Schidrowitz, S. S. Pickles, D. F. Twiss, G. Gallie, T. R. Dawson, E. A. Murphy, H. Green; also W. W. Vogt and R. D. Evans, *Ind. Eng. Chem.*, **15**, 1015 (1923); Schippel, *J. Ind. Eng. Chem.*, **12**, 33 (1920).

[349] See, for example, J. T. Blake, *Ind. Eng. Chem.*, **20**, 1084 (1928) and also L. Hock and G. Fromandi, *Kautschuk*, **5**, 81 (1929).

† Translator's Note. See B. B. Evans [*India Rubber J.*, **64**, 815 (1922)], E. C. Zimmerman [*Rubber Age*, **12**, 130 (1922)], and W. W. Vogt and R. D. Evans [*Ind. Eng. Chem.*, **15**, 1015 (1923)] for the effect of isotropic and anisotropic powders on rubber mixtures. — N. A. S.

[350] *Ind. Eng. Chem.*, **20**, 1084 (1928); also *Gummi-Ztg.*, **43**, 649 (1928).

‡ Translator's Note. Blake, however, was far from being in agreement with Wiegand with respect to reinforcement. He contended that no filler, not even carbon black, really enhances the strength of vulcanized rubber. It was his view that the reinforcing effect is only an "apparent" one and he attempted to prove this by means of Wiegand's own data. The erroneous nature of this conclusion has been discussed by both N. A. Shepard [in J. A. Alexander's "Colloid Chemistry," Vol. IV, p. 313, **1932**] and P. Schidrowitz [*India Rubber J.*, **76**, 1071 (1928)].—N. A. S.

[351] *India Rubber J.*, **73**, 31 (1927); refer also to the work of this author on the influence of pigments in *Ind. Eng. Chem.*, **17**, 939 (1925).

§ Translator's Note. Blake's calculation of this amount is obviously incorrect, as it was based upon the assumption of an average particle size for carbon black which is several times that now accepted. [*Cf.* N. A. Shepard, in J. Alexander, "Colloid Chemistry," Vol. IV, p. 332, **1932**].—N. A. S.

[352] See C. C. Loomis and H. E. Stump, *Chem. Met. Eng.*, **29**, 540 (1923), *India Rubber World*, **68**, 763 (1923) or E. A. Hauser, *Inst. Rubber Ind. Trans.*, **2**, 226 (1926) and *Kautschuk*, **3**, 2 (1927); also the monograph of this author on "Latex," p. 133, Steinkopff, Dresden and Leipzig, **1927**.

[353] M. LeBlanc, M. Kröger and G. Kloz: "The Adsorptive Properties and the Particle Sizes of Different Carbon Blacks in Organic Solvents and in Crude Rubber Mixes," *Kolloidchem. Beihefte*, **20**, 356 (1925). M. Pavlenko and P. Nasarov, *Russ. J. Chem. Ind.*, **4**, 642 (1927), worked along similar lines; *cf. Chem.-Zentr.*, **99**, I, 593 (1928); *Chem. Abstracts*, **22**, 4006-7 (1928). LeBlanc and his co-workers found that uncured carbon black mixes in benzene give sols which have different viscosities, depending upon the nature of the black. An uncured carbon black—rubber mix containing a good black characteristically has a smaller dispersibility in benzene and the cement formed has high viscosity; with bad blacks just the reverse effects are obtained.** With respect to the mechanism of reinforcement, see LeBlanc and Kröger, *Z. Electrochem.*, **34**, 725 (1928).

** Translator's Note. It is rather unusual to

P. Stamberger [354] on the solubility of mixes fit in here. Added in higher concentration, carbon black prevents the swelling of crude rubber to a large extent; in low concentration, it has little influence. In a dissolved condition, there is a certain adsorption of the filler by the rubber, as if the strength of cohesion (of the rubber) were then of a much lesser magnitude than in the absence of a swelling medium, bringing about an increase in the strong van der Waal's forces, with which the active filler and the rubber are held together (compare also the following section).† In conclusion, a few literature references [355] along a somewhat different line are given.

Thermodynamic Theory of Filler Action

Hock [356] has further developed, along theoretical lines, the views resulting from the investigations mentioned above, and at the same time has worked out a calorimetric method of estimating the surface energy between rubber and fillers. The heat of swelling of unvulcanized mixes was observed, closely following the previously described method used in measuring the Joule effect. If, for example, a mixture of rubber and zinc oxide is swelled in benzine, there results, on the one hand, swelling of the rubber and, on the other hand, wetting of the particles of filler by the benzine. These changes are accompanied by heat effects, which may be separately estimated for the pure rubber on the one hand, and for the filler on the other. Then the effect to be expected from the amount of rubber and from the amount of filler present can be calculated, provided there is no energy consumed during the swelling in

use the terms "good" and "bad" in connection with the blacks used in rubber compounding. The author apparently wishes to distinguish blacks of "high" and "low" reinforcing power. It is not true that a black of low or moderate reinforcing effect is necessarily a "bad" black. There are applications in which such a black may be decidedly more useful than a high grade rubber channel black of "good" reinforcing action. — N. A. S.

[354] *Kolloid-Z.*, **42,** 295 (1927); **45,** 239 (1928); also *Rec. trav. chim.*, **47,** 316 (1928); *Rubber Age (N. Y.)*, **23,** 321-2 (1928).

† Translator's Note. That the effect of a reinforcing pigment on the swelling tendency or solubility of rubber persists even after the pigment has been removed, has been reported by F. B. Menadue [*India Rubber J.*, **85,** 689-92, 717-722 (1933); **86,** 23-26, 53-56 (1933)]. By mixing acid-soluble pigments, such as magnesium carbonate or zinc oxide, in large volume into rubber, and then removing the carbonate or oxide by treating with ether-acetic acid, he found the residual rubber to be markedly changed as regards solubility in such solvents as benzene or petroleum ether. Such rubber is called "Diphase" by Menadue, as it can be separated into two distinct solubility fractions. — N. A. S.

[355] The following publications treat of fillers and their action: C. R. Johnson on the chemistry of gas black, with special reference to its content of volatile matter, *Ind. Eng. Chem.*, **20,** 904 (1928). The adsorption of oxygen on gas black also plays a part, as D. J. Beaver and T. P. Keller have shown, *Ind. Eng. Chem.*, **20,** 817 (1928). Reclaimed rubber can also be reinforced, as H. A. Winkelmann and E. G. Croakman showed in *Ind. Eng. Chem.*, **20,** 134 (1928); however, the reinforcing action is much less in this case (see p. 429, footnote 120). Since Wiegand's pioneer work, many rubber technologists have worked on the practical application of reinforcing fillers. Only a few can be mentioned here. F. Evers, "Sedimentation Analysis of Fillers," *Kautschuk*, **3,** 70 (1927); F. Kirchhof, "Estimation of Fineness," *Kautschuk*, **1,** 17 (Sept., 1925). For the work of H. Pohle in the microscopic field see page 637 in this book; also *Z. wiss. Mikroskop.*, **44,** 183 (1927), *Gummi-Ztg.*, **41,** 2755-6 (1927); also the microscopic studies of E. A. Grenquist, *Ind. Eng. Chem.*, **20,** 1073 (1928). For the x-ray estimation of particle size, see B. Davis, *J. Franklin Inst.*, **204,** 29 (1927). The dispersoid analysis of barium sulfate is treated of by J. C. Shepherd, *Ind. Chem.*, p. 57 (Feb., 1917), referred to in *India Rubber J.*, **73,** 703 (1927), and T. R. Dawson and N. H. Hartshorne, *India Rubber J.*, **73,** 885, 926, 961 (1927). Yutaka Tanaka evaluated magnesium carbonate as a filler in *Inst. Rubber Ind. Trans.*, **2,** 330 (1927); T. J. Drakeley and W. F. O. Pollett published a study on china clay as a reinforcing agent, *Inst. Rubber Ind. Trans.*, **4,** 424 (1929). We conclude this incomplete enumeration by referring to a recent, comprehensive investigation of active fillers by R. W. Lunn in *Inst. Rubber Ind. Trans.*, **4,** 396 (1929), in which, as the author also did with advantage (see next section), the reinforcing effect is related to the unit volume of the filler and is clearly presented as dependent upon its concentration. Concerning stearic acid, see R. P. Dinsmore and W. W. Vogt, *Inst. Rubber Ind. Trans.*, **4,** 85 (1928).

[356] L. Hock and S. Bostroem, *Gummi-Ztg.*, **41,** 1114, 1165 (1926); L. Hock, *Kautschuk*, **3,** 207 (1927), and also dissertations of S. Bostroem, *Kolloidchem. Beihefte*, **26,** 439 (1928); and of F. Hartner, Giessen, **1929**; *Kolloidchem. Beihefte*, **30,** 83 (1929); *Rubber Chem. Tech.*, **3,** 215 (1930).

overcoming the strength of adhesion of the rubber and filler, which results in an additional, negative heat effect. The difference between the calculated heat effect and that observed during the swelling of the filler-rubber mixture gives, according to the Hess law,[357] the value for the heat of adhesion, which results from the wetting of the rubber and filler. Of course, since the wetting effect is reversed in the presence of the benzine, the sign is negative.

If the surface contacts are broken by the application of mechanical work, the absorption of latent heat from the surroundings also must be considered. Just as in the formation of a square centimeter of water surface, not only must 73 ergs of work (surface tension of water $\sigma = 73$ dynes/cm.) be supplied for potential energy, but also a certain amount of heat must be absorbed from the surroundings. This amount of heat (approximately 10^{-6} cal.) is, moreover, of the same order of magnitude as the surface energy itself (73 ergs = approx. 1.7×10^{-6} cal.). In estimating the work of adhesion calorimetrically, the external work does not have to be considered, and there is directly obtained from the measurement, a change in total energy, which may be represented by U. If the mechanical work of separation is designated as A, in which case A [358] is the product of the surface tension and the area of the contact surface f of the rubber and filler, then the thermodynamic relation between the calorimetrically estimated total surface energy U and the free energy A, which is accountable for the increase in work capacity, is given by the Gibbs-Helmholtz equation:

$$\sigma f - U = T \frac{d \sigma f}{dT} \tag{28}$$

In two-phase systems, the rule is very frequently confirmed that the free energy, available in a given case as maximal work, amounts to approximately half (in any case to a large fraction) of the total surface energy, corresponding to a negative temperature coefficient of surface tension of a few tenths of a per cent. If this result is applied experimentally to the rubber-filler system, it is to be expected that the increase in work capacity, caused by the incorporation of an active filler in a definite amount of rubber, may be estimated from the value of the heat of adhesion U.

It must further be taken into consideration that only a certain proportion of the rubber is in actual surface contact with the filler, since the wetting is naturally incomplete as a result of agglomeration, etc., and the wetting probably is the more incomplete, the greater the concentration of the filler in the rubber. The heat of wetting of rubber and filler, calculated to 1 gram of dispersed filler, must therefore give different values at different concentrations and approach a maximum value at infinite dilution, at which the assumption of complete wetting of the surface of the particles is permissible.

The calculation of the heat of wetting of rubber and an active carbon black, as carried out by Fritz Hartner at the suggestion of the author, is a concrete example. This calculation was made from the following experimental data. A simple unvulcanized mixture consisting of 85 per cent rubber and 15 per cent black was used, for in general this method, which is still in the development stage, must be confined to simple mixtures before being applied to the more complicated systems. From the heat of swelling of rubber, -0.1

[357] *Cf.* Textbook of J. Eggert, p. 264 (*see* footnote 71, p. 413, of this book).

[358] This is, as follows from the later work on the subject, only an ideal and simplifying assumption, in which the work of friction is not taken into account. *Cf.* also L. Hock, *Kautschuk*, **4**, 165 (1928) and *Z. Electrochem.*, **34**, 662 (1928); also *Rubber Chem. Tech.*, **2**, 275-7 (1929).

cal./gram, and the heat of wetting of the black, + 2.8 cal./gram, the heat of swelling for the mixture of the above composition can be calculated, without considering the heat of adhesion which must also be determined. Using benzine as the swelling agent, the heat of swelling of the mixture is $-0.85 \times 0.1 + 0.15 \times 2.8 = +0.335$ cal./gram. However, a heat effect of — 0.35 cal. was observed. The difference of 0.685 calories thus corresponds to the total surface energy between rubber and black, which had to be overcome in order to bring about their separation. Per gram of black, there is thus $U_{15} = +4.53$ * calories of heat of wetting by rubber.

The U value, down to the minimum concentration, may be determined in a similar manner, so that finally it is possible to approximate more or less accurately, through extrapolation, the heat of wetting U_o at infinite dilution, which may be considered as a characteristic constant for each system concerned. Estimations of this kind have been carried out by Hartner. Figure 104 illustrates the dependence of the specific heat of wetting upon the concentration of the filler. With the value U_o determined, a conclusion concerning the completeness of the dispersion can be drawn from the relationship U_c/U_o, and it is thus possible to obtain an idea of the quality of the mix

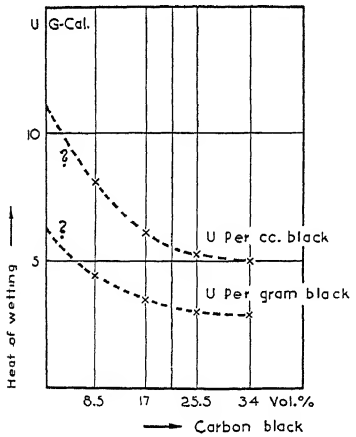


Figure 104—Specific heat of wetting of carbon black and rubber in relation to the concentration of the fillers.
(According to L. Hock and F. Hartner.)

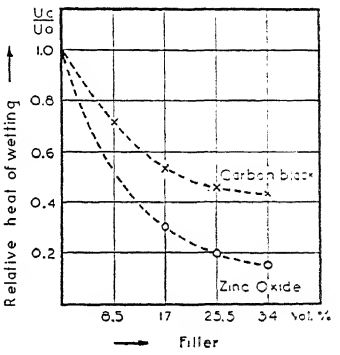


Figure 105—Relative specific heats of wetting of rubber and fillers in relation to the degree of dilution.
(According to L. Hock and F. Hartner.)

from the standpoint of the distribution of the filler. Thus, Figure 105 gives an insight into the relative utilization of the surface energy of carbon black and zinc oxide mixings at different concentrations of filler. It should be pointed out that the extrapolation to the value U_o ought to be checked by further, still more reliable, measurements.[359]

If, as already mentioned above, the increase in the work capacity of any given rubber mixture is considered identical to the free surface energy A of the system, which is defined not only by the capacity factor f, but also by the

* Translator's Note. This means that 4.53 cal./gram of heat were evolved. In the English system of thermodynamic nomenclature U_{15} would be expressed not as *plus* 4.53 cal./gram, but as *minus* 4.53 cal./gram. — N. A. S.

[359] Planned by the Giessen Physical-Chemical Institute.

intensity factor σ, then its numerical value follows from the experimental determination of the work capacity. It should again be emphasized that with an increasing amount of filler that is not ideally mixed, but functions solely as ballast, there is also a work of friction to be overcome, which has nothing to do with the free surface energy sought. Again, by extrapolation of the different values of A_c to infinite dilution, the amount A_o for the free surface energy of the ideally diluted mixture may be calculated approximately.[360] With the above mixture, for which $U_{15} = 4.53$ calories per gram of carbon black, the increase in work capacity may be calculated from the following data: work capacity of the crude rubber alone 0.296 cal./cc. (recalculated from mechanical into caloric measure; *see* footnote on page 500), of the mixture 0.418 cal./cc.; reinforcement consequently 0.122 calories, or, recalculated to the amount of crude rubber in the mixture (91.5% by volume): 0.15 calories, attributable to the amount of black contained in 1 cc. of the mixture.

The more detailed measurements which have been made up to the present have shown the expected value 0.5 for the ratio A_o/U_o for the rubber-filler system.[361] If the specific surface of the filler in question is known from microscopic measurement of the average particle size, it is possible to calculate the interfacial tension between rubber and filler in absolute figures.[362]

The procedure described makes possible, therefore, assertions concerning the mechanical behavior of a mixture from the purely calorimetric estimation of the heat of swelling. A way is thus shown of handling the problem of the strength of simple rubber mixes fundamentally from the standpoint of thermodynamics.*

While an evaluation of U_o which is free from objection can be made calorimetrically, the determination of A_o by dynamometric means is beset with many difficulties. These are not only of a technical, but also of a fundamental nature, especially since the stresses in rubber under tension are different when a rubber mixture is ruptured than when rubber itself (i.e., without pigmentation) is ruptured.[363] In this connection an instructive study by LeBlanc and Kröger on tear-resistance and grain effect leads to the conclusion that the addition of fillers puts rubber at lower temperatures in a condition similar to that produced by ordinary vulcanization.

The difficulty in determining A_o experimentally can be avoided if one and the same substance, in three different degrees of fineness, is applied as the filler and provided reliable assertions can be made concerning the relative sizes of the specific surfaces of the three samples, as for example, by determining their relative heats of wetting in a liquid. Then there are three series of

[360] For the method of carrying out the graphic calculation, see the separate examples in the above-mentioned dissertation of F. Hartner, *Kolloidchem. Beihefte*, **30**, 83 (1929); *Rubber Chem. Tech.*, **3**, 215 (1930).

[361] This number is naturally only an approximation.

[362] In this way, Hartner arrived at a preliminary determination for carbon black-rubber of 140 ergs/cc. of black. See the above-mentioned dissertation; *Rubber Chem. Tech.*, **3**, 215 (1930).

* Translator's Note. F. A. Steele [*Physics*, **1**, 101 (1931)] takes strong exception to the assumptions of Hock and Hartner. A critical discussion of this whole subject was included in the paper by N. A. Shepard, C. R. Park and J. N. Street on "Fillers and Reinforcing Agents," read at the fall meeting of the Rubber Division, American Chemical Society, Chicago, Ill., September, 1933.—N. A. S.

[363] For greater detail, see also F. Hartner, *Kolloidchem. Beihefte*, **30**, 83 (1929); *Rubber Chem. Tech.*, **3**, 215 (1930), and especially LeBlanc and Kröger, *Z. Electrochem.*, **34**, 725 (1928). Mention should also be made of the work of W. Cecil Davey in *J. Soc. Chem. Ind.*, **45**, 364T (1926), in which the opinion is expressed that the incorporation of fine pigments in rubber produces effects on the elasticity, swelling, etc., similar in certain respects to those brought about by vulcanization. Also P. Schidrowitz, in *J. Oil Colour Chem. Assoc.*, **9**, 208-10 (1926); *Inst. Rubber Ind. Trans.*, **2**, 89 (1926), points out the influence of the particle shape of a filler on the mechanical properties of a mix *before* vulcanization.

mixes to be investigated, the value U_o to be ascertained as definitely as possible through graphic extrapolation, and the following three equations with three unknowns to be solved:—

$$\begin{aligned} 1)\quad & \sigma f = k U_{o\,1} \\ 2)\quad & \sigma n f = k U_{o\,2} \\ 3)\quad & \sigma m f = k U_{o\,3} \end{aligned} \tag{29}$$

The surface tension σ is assumed to be identical for all three powders. This assumption is certainly correct in the case of zinc oxide.[364] The factors n and m result from the relative degrees of dispersibility of the three powders.[365] The constant k gives the relationship of free to total surface energy for the system in question and may thus be calculated without conducting a mechanical tensile test (which gives a k value of approximately 0.5 as already mentioned). The letter f represents the specific surface of the powder. If the heat effect U_o is calculated in ergs, the surface tension of rubber to filler may be computed directly in dynes/cm. If the factor k for a given filler has also been ascertained in the designated and purely calorimetric manner, it is possible, through an experimental determination of A_o, to find out what part of the observed reinforcement depends entirely on the friction of the filler, etc., and what part is due to the surface energy, and thus which is the more ideal filler. If an incorporation of filler up to the limit of saturation were possible, the curve representing the relationship between work capacity and filler concentration, in such a perfect mixture, would be, up to a certain limit, a continuously rising straight line, and would not, as is the case with actual mixings containing fillers of increasingly inert character, rapidly develop a maximum. Figure 106 represents the reinforcing effect of a filler in an actual and in such an "ideal" mix.

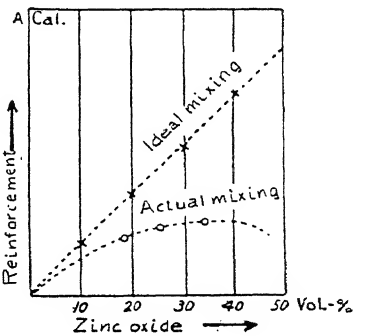


Figure 106—Diagrammatic representation of the reinforcement produced by a filler in the case of an "ideal mixing."

(According to L. Hock.)

Since the above ideas concerning the theories of rubber-filler behavior are drawn from a field of investigation which is still in the development stage, it must suffice here to refer only to the fundamental views and to discuss the experimental evidence which supports them. A critical discussion and evaluation of the investigations described would lead too far here; for this reason the reader must be referred to the original literature.

[364] With carbon blacks, made by different methods, the chemical nature of the surface is in each case different, and such a supposition is permissible only with reservations.

[365] *Cf.* L. Hock and S. Bostroem, *Gummi-Ztg.*, **41**, 1112 (1927). For further literature on the determination of degree of dispersibility, *cf.* L. Hock, *Kautschuk*, **4**, 266 (1928) and F. V. v. Hahn, "Dispersoid Analysis," Steinkopff, Dresden, **1928.**

The rubber technologist is indebted especially to H. Pohle [366] for contributions to the solution of filler problems through microscopical studies. In an interesting manner, other investigators, especially LeBlanc and his collaborators, sought to contribute to the explanation of specific filler action through investigation of the "solubility" of rubber-carbon black mixtures. The work of Stamberger on the sedimentation of fillers from benzene solutions of rubber mixtures is related to this. These investigations have already been mentioned at the beginning of this chapter.

Besides acting in the capacity of a dispersing medium for solid substances, rubber can behave as a true solvent. This is of special importance with respect to the action of the sulfur, which acts as the curing agent. C. O. Weber [367] proved that sulfur dissolves in rubber. He obtained, as did also H. Loewen [368] later, a microscopically translucent system from sulfur and rubber when hot, out of which, on cooling, the sulfur separated in the form of small droplets. H. Skellon [369] thoroughly investigated this same problem, as did also Loewen later. In their work, it was shown that the solubility of sulfur in vulcanized rubber is greater than in raw rubber. This increase in solubility with increasing coefficient of vulcanization was confirmed by C. S. Venable and C. D. Greene.[370] Considering the problem from an exact physico-chemical standpoint, W. J. Kelly and K. B. Ayers [371] sought to decide the question of the state in which the sulfur exists in the rubber. They investigated the validity of Nernst's distribution law * in the sulfur-rubber system. For this purpose they first placed a rubber-sulfur mix in amyl alcohol and determined the distribution of the sulfur between the two solvents. They then obtained the same equilibrium, approaching it from the other side by placing different amounts of rubber in a saturated solution of sulfur in amyl alcohol. In both cases the ratio of the concentration of the sulfur in the alcohol to that in the rubber was constant. From this, the conclusion is reached that it is a case of true solution, in which the sulfur must be in a similar molecular condition in both media (*see also* p. 511). At 30° C. approximately 1 per cent of sulfur dissolves in raw rubber. Vulcanized rubber with a vulcanization coefficient of 17 (*see* p. 392) can dissolve about 5 to 6 per cent of sulfur at 75° C. This problem has more recently been discussed by D. F. Twiss.[372]

G. Bruni [373] has investigated the solubility of other crystalline substances in rubber. He has shown that rubber behaves like a liquid † towards naphthalene, azobenzene and paratoluidine. Its solvent power is greatest for aromatic compounds, less for hydrocarbons and their halogen derivatives, still less for aliphatic compounds, and least for inorganic substances.‡

[366] *Cf.* section on "Microscopy of Technical Vulcanizates," in this book, and also *Z. wiss. Mikroskop.*, **44**, 183 (1927); *Gummi-Ztg.*, **41**, 2755-6 (1927).

[367] *Gummi-Ztg.*, **18**, 93, 342 (1904).

[368] *Kolloid-Z.*, **27**, 744, 923, 1301, 1647 (1913); *Kautschuk*, **4**, 243 (1928). Further, Erich Kirsch describes the formation of a very extraordinary crystalline appearance of sulfur in rubber in his dissertation carried out at the suggestion of Linck, Jena (1928); *Z. anorg. allgem. Chem.*, **174**, 57-60 (1928). For the separation of sulfur by light, see H. Pohle, p. 646 of this book and also *Naturwissenschaften*, **15**, 162 (1927).

[369] *India Rubber J.*, **46**, 251 (1913).

[370] *J. Ind. Eng. Chem.*, **14**, 319 (1922).

[371] *Ind. Eng. Chem.*, **16**, 148 (1924).

* Translator's Note. Or Henry's law. W. J. Kelly and K. B. Ayers did not mention Nernst, apparently preferring to refer back to the earlier law. — N. A. S.

[372] *Inst. Rubber Ind. Trans.*, **3**, 386 (1928).

[373] *Giorn. chim. ind. appl.*, **3**, 51 (1921) and also *Atti. accad. Lincei* (5), **30**, I, 75-80 (1921).

† Translator's Note. Forming true saturated solutions. — N. A. S.

‡ Translator's Note. A more exact translation from the Italian is as follows: Such solvent power is maximum for aromatic organic substances and, in general, for the hydrocarbons and halogenated derivatives, less for most of the substances of the aliphatic series, especially those that are oxidized, and least for the greater part of the inorganic substances, with the exception of certain of the elements. —N. A. S.

Rubber as a Solvent for Liquids and Gases

Since swelling of the rubber gel occurs in the production of rubber solutions, the rubber may be considered as the solvent for the swelling liquid—or even for its vapor—equally as well as it may be viewed as the solute. What has been stated in the chapter on swelling and solution should be referred to in this connection.† However, special mention should be made of the work of F. W. Küster,[374] who studied the distribution of ether between rubber and water, in order to test the Nernst partition theory. As the result of this investigation, the rubber is now to be regarded as the solvent. The observed conformity with the theory was quite similar to that which Nernst[375] had established for the distribution of phenol between benzene and water. The ratio between the concentrations of ether in water and in rubber is not constant, and differs in this respect from the case where the distribution of a substance is between two media with the same molecular weight. There is also no such constant relationship between the concentration of ether in water and the square root of its concentration in rubber as there would be if the ether dissolved in the rubber in the form of double molecules. It appears much more as though the numerical relationship mentioned above had a strong tendency to change with increasing concentration of ether dissolved in the rubber, so that the conclusion must be drawn that there is a condition of association of the ether in the solvent rubber, varying with the concentration. Table 15 gives the figures obtained by Küster at 18° C. C_K is the concentration of ether in rubber (grams in 100 cc. of solution) and C_W its concentration in water (also in grams per 100 cc. of solution).

TABLE 15.—*Distribution of Ether Between Rubber and Water at 18° C. (F. W. Küster).*

	C_K	C_W	C_K/C_W	$\sqrt{C_K/C}$
1.	3.85	1.24	3.10	1.58
2.	7.96	2.34	3.42	1.21
3.	16.14	4.26	3.79	0.94
4.	20.12	5.07	3.97	0.88
5.	24.49	5.66	4.33	0.87
6.	28.82	6.37	4.40	0.83
7.	31.43	6.99	4.50	0.80
8.	35.09	7.40	4.74	0.80
9.	38.09	7.93	4.80	0.78
10.	49.18	9.18	5.36	0.76

The absorption of water by rubber has also been repeatedly studied, especially from a technical standpoint. The work of F. Kirchhof[376] and of C. R. Boggs and J. T. Blake[377] should be especially mentioned.* Finally, an investigation by H. H. Lowry and G. T. Kohman[378] should be discussed. This was concerned with the extent and speed of water absorption by raw and vulcanized rubber over sodium chloride solutions of different vapor pressures at different temperatures. At 25° C. the solubility of water vapor in rubber is proportional to its partial pressure, up to a vapor pressure of

† Translator's Note. See also P. Stamberger, *Rec. trav. chim.*, **47**, 316 (1928); *Kolloid-Z.*, **45**, 239 (1928) and *Rubber Age (N. Y.)*, **23**, 321 (1928); J. R. Scott, *Inst. Rubber Ind. Trans.*, **5**, 95 (1929); Wo. Ostwald, *Kolloid-Z.*, **49**, 60 (1929); and "The Action of Solvents on Vulcanized Rubber," Vanderbilt News, **1**, No. 2, p. 5 (1931). — N. A. S.

[374] *Z. physik. Chem.*, **13**, 445 (1893).

[375] *Z. physik. Chem.*, **8**, 110 (1891).

[376] *Kolloid-Z.*, **35**, 367 (1924).

[377] *Ind. Eng. Chem.*, **18**, 224 (1926).

* Translator's Note. This subject has recently received much attention. See S. J. Skinner and T. J. Drakeley, *Inst. Rubber Ind. Trans.*, **7**, 196 (1931). See also D. H. Andrews and J. Johnston, *J. Am. Chem. Soc.*, **46**, 640 (1924); S. E. Hill, *Proc. Soc. Exptl. Biol. Med.*, **26**, 590 (1929); E. E. Schumacher and L. Ferguson, *Ind. Eng. Chem.*, **21**, 158 (1929); H. A. Winkelmann and E. G. Croakman, *Ind. Eng. Chem.*, **22**, 1367 (1930); and K. J. Soule, *Ind. Eng. Chem.*, **23**, 654 (1931). N.A.S.

[378] *J. Phys. Chem.*, **31**, 23 (1927).

about 16 mm. of mercury. At higher vapor pressures, it is greater, as would be expected from Henry's law.§ The volume increase in the rubber is practically identical with the volume of water absorbed. Besides the formation of a true solution of water in rubber, it must also be assumed that solution of the water-soluble substances contained in the rubber occurs. If the water absorption takes place directly from the liquid phase, then the amount is just as great as if the absorption had taken place from the vapor phase at the same partial pressure, provided there are no secondary influences. With increasing combined sulfur content, the water absorption passes through a maximum (at about 7 per cent of sulfur). The speed of solution increases with the temperature. No further general laws have been established. In an investigation on some synthetic dimethyl rubbers, H. Pohle [379] reported the vapor tension equilibria of some dispersions of rubber in water and also in benzene.

Finally, rubber may also serve as a solvent for gases. The permeability of rubber to such gases was exhaustively studied by Graham [380] many years ago. Aside from studies on the perviousness of rubberized fabrics to gases [381] (important in aeronautics, but less fruitful from a physical standpoint, so that it is sufficient merely to mention them here), there has appeared in recent times only one investigation (with supplements) which solves the problem satisfactorily from a theoretical standpoint. This is the work of H. A. Daynes [382] who observed the diffusion of hydrogen and other gases through a membrane of pure vulcanized Para rubber 0.03 to 1.6 mm. in thickness. On the opposite side of the membrane, in these experiments, there was in some cases another gas, in others a vacuum. True diffusion according to the law of Fick must be distinguished from a certain perviousness due to porosity. This can be done quantitatively only by carefully considering the accompanying processes, and especially by taking into account the initial saturation of the membrane with the gas. If this is done, it is possible to demonstrate a diffusion gradient within the membrane so that at every point a well defined concentration of hydrogen, for example, can be assumed. The diffusion constant for hydrogen, as determined by Daynes, was 11.4×10^{-6} cm./sec. at 20° C.; the absorption coefficient, also at 20° C. and at atmospheric pressure, was 0.035. The latter has only a relatively small temperature coefficient of 0.5 per cent per degree, while that of the diffusion coefficient is considerably greater.

The following information on the relative permeabilities ($H_2 = 1$) of rubber films is taken from the work of Daynes:*

Air	0.21	NH_3	11.3	A	0.20	AsH_3	1.3
CO_2	2.46	CO	0.20	$(CN)_2$	10	C_2H_4	1.3
He	0.31	H_2	1.00	CH_4	0.39	N_2	0.18
N_2O	4.53	O_2	0.46	H_2S	13	H_2O(gas)	47

§ Translator's Note. This was incorrectly translated into the German from the English. What H. H. Lowry and G. T. Kohman actually stated was: "Above a certain vapor pressure (approx. 16 mm. at 25° C.), the solubility no longer obeys Henry's Law, but is much greater than the law would predict." —N. A. S.

[379] *Kolloidchem. Beihefte*, **13**, 1 (1920).

[380] *Phil. Mag.* (3), **2**, 175, 269, 356 (1833); (4), **32**, 401 (1866); *Pogg. Ann. Physik*, **28**, 331 (1833); **129**, 549 (1866). *Cf.* also Mitchell, *J. Royal Inst.*, **2**, 101, 307 (1831), and also *Pogg. Ann. Physik*, **129**, 550 (1866), and Wroblewski, *Wied. Ann. Physik*, **2**, 481 (1877); **4**, 268 (1878); **7**, 11; **8**, 29 (1879).

[381] See F. W. Hinrichsen, "Das Materialprüfungswesen." p. 503, Enke, Stuttgart, **1912**; also W. Frenzel, *Chem.-Ztg.*, **43**, 530 (1919); Heyn, *Sitzber. preuss. Akad. Wiss.*, **14**, 365 (1911).

[382] *Proc. Roy. Soc. (London)*, **A97**, 286 (1920); *Inst. Rubber Ind. Trans.*, **3**, 428 (1928).

* Translator's Note. *Cf.* also W. C. Davey and T. Ohya, *Trans. Inst. Rubber Ind.*, **5**, 27 (1929). See K. Kanaka [*Bull. Chem. Soc. Japan*, **3**, 183 (1928)] for the permeability of rubber mixings to hydrogen.—N. A. S.

The relative absorption coefficients ($CO_2 = 1$) for a series of gases are as follows:

He	< 0.1	H_2	< 0.1	N_2	0.035	CO	0.036
O_2	0.074	CH_4	0.255	CO_2	1.0	C_2H_4	1.43
H_2S	2.70	NH_3	9.39	SO_2	19.7		

For the temperature coefficients of diffusion, the following values, valid for the temperature range 15° to 25° C., were determined:

CO_2	+ 5.9%	per degree	Celsius	(or	Centigrade)
Air	6.7%	"	"	"	"
N_2	7.7%	"	"	"	"
H_2	5.0%	"	"	"	"
He	5.1%	"	"	"	"
O_2	6.3%	"	"	"	"

In the higher temperature range, the following values for the increase in diffusion obtain, with the value at 20° C. placed at 1.0:

	20° C.	70° C.	100° C.	140° C.
(1) For H_2	1.00	4.4	8.8	32 (estimated)
(2) For CO_2	1.00	4.2	6.3	24 (estimated)

In the extensive work of Daynes, there is also information on the absorption of water by rubber and on the drying of rubber. The work of J. D. Edwards and S. F. Pickering [383] also gives a large number of numerical values.

Lastly, there should be mentioned from Graham's well-known investigations on the diffusion of gases through rubber membranes (a phenomenon which was first pointed out by Mitchell in 1837), that the velocity of diffusion (*in vacuo*) is to a great extent dependent on the nature of the gases, but not in so simple a manner as in the case of diffusion through porous partitions, where the velocity is dependent on the gas density. In the case of rubber, there is a specific dependence on the chemical nature of the gases involved and, above everything else, on their solubility in rubber. If the diffusion velocity of nitrogen is taken as 1.0, then that of carbon monoxide amounts to 1.11, of methane to 2.15, of oxygen to 2.56, of hydrogen to 5.50, and of carbon dioxide, in spite of its great density, to 13.59. If air is passed through a rubber membrane, the air increases in oxygen content to a remarkable extent, since the nitrogen diffuses only slowly.*

Rather comprehensive studies have been carried out on the solubilities of different kinds of gases in rubber vulcanizates of varied composition.† These, however, have led to no new physical points of view. The conspicuous solubility of carbon dioxide, and especially of ammonia and sulfur dioxide, in

[383] *Bur. Standards Sci. Paper,* **No. 387,** July 12, 1920; also in condensed form in *Chem. & Met. Eng.,* **23,** 17, 71 (1920). V. Rodt, [*Chem.-Ztg.,* **38,** 1249 (1914)], reports on the influence of moisture on the permeability of rubber to carbon dioxide. Dubosc studied the adsorption, absorption, and diffusion of different gases in contact with raw rubber, vulcanized rubber, and balloon fabrics, *Rev. gen. caoutchouc,* **5,** No. 39, p. 7 (1928). In an original way, S. E. Hill [*Science,* **67,** 374 (1928); *India Rubber J.,* **75,** 710 (1928); and also *Gummi-Ztg.,* **42,** 2253 (1928)] has estimated the diffusion of oxygen through rubber, by using as indicator phosphorescent bacteria, which just phosphoresce at a partial pressure of oxygen of 5.3×10^{-3} mm.

* Translator's Note. The "Permeability of Rubber to Air," has been the subject of careful study by V. N. Morris and J. N. Street [*Ind. Eng. Chem.,* **21,** 1215 (1929); **23,** 837 (1931)], who obtained results confirming the evidence that the temperature coefficient of permeability is relatively high. They also found that under certain circumstances moisture slightly decreased the permeability of rubber to air, although prolonged immersion of vulcanized rubber in water resulted in an appreciable increase in permeability. Their results indicated further that permeability varies inversely with the thickness of the rubber and with the volume of compounding ingredients present; that it is increased by stretching the rubber; and that it is influenced but slightly by milling, by the kind of crude rubber used, and by the temperature of vulcanization. — N. A. S.

† Translator's Note. See the recent work of I. Williams and A. M. Neal on the solubility of oxygen in rubber, *Ind. Eng. Chem.,* **22,** 874 (1930). — N. A. S.

rubber, has been established.[384] G. Tammann and K. Bochow [385] investigated the absorption in rubber of hydrogen under high pressure, and the behavior on reducing the pressure. The hydrogen was generated from zinc and sulfuric acid, under a pressure of 550 kg./sq. cm., in the presence of vulcanized rubber. For 48 hours, the hydrogen was abundantly absorbed by the rubber, with volume increase. Even 15 to 20 minutes after releasing the pressure, the rubber retained 2 to 3.5 times its volume of gas. It may be that the absorption coefficient of the rubber for H_2 is approximately independent of the pressure. Interesting and older investigations on the absorption of gases are described in O. Lehmann's "Molekularphysik." [386]

Since, as previously mentioned, rubber possesses the properties of a solvent, it can be used as a semi-permeable membrane in osmosis experiments (Nelson,[387] Koenig [388]) or can serve as a dialyzing membrane (Ostwald,[389] Michaelis [390]). Reference to these possibilities must suffice here.

[384] C. S. Venable and Tyler Fuwa, *J. Ind. Eng. Chem.*, **14**, 139 (1922). See also contributions to this subject by F. Kirchhof in "Fortschritte in der Kautschuktechnologie," p. 187, Th. Steinkopff, Dresden and Leipzig, **1927.**

[385] *Z. anorg. allgem. Chem.*, **168,** 322 (1928).

[386] Vol. 2, p. 123, Wilhelm Engelmann, Leipzig, **1889.**

[387] *J. Am. Chem. Soc.*, **35,** 658 (1913); osmotic pressures of organic compounds dissolved in pyridine determined through the use of a rubber membrane; also of solutions of lead nitrate and especially of dextrose in pyridine.

[388] *J. Phys. Chem.*, **22,** 461 (1918); osmotic pressures of cane sugar, silver nitrate, etc., in pyridine. Dental dam as a semi-permeable membrane.

[389] Wo. Ostwald and P. Wolski, *Kolloid-Z.*, **28,** 228 (1921).

[390] L. Michaelis and S. Dokan [*Biochem.-Z.*, **162,** 258 (1925)] studied, among other things, electrical phenomena and ion-permeability, using membranes of rubbe dipped in rubber solutions).

Physical Testing Methods

By K. Memmler and A. Schob *

Rubber has achieved far-reaching application in almost all branches of modern industry because of its physical characteristics. These are essentially solidity, mutability, elasticity, insulating property, etc. Attention has turned to the testing of rubber by these properties to at least as great an extent as to testing by chemical analysis; and the results obtained by the physical testing of rubber have won importance as standards of comparison. To be sure, many years of painstaking effort were required to develop methods which enjoyed universal recognition and obtained entrance into the laboratories of the rubber industry. Formerly there were chemists working in these laboratories who had a definite prejudice against all tests of quality which were not based strictly on chemical analysis. In the few laboratories which began using physical tests, there was at first too great a restriction to the practical needs of particular rubber goods.

Although not heeded in the first physical tests, experience in the development of test procedures with other substances had long taught that the salient points in testing are simplicity, certain reproducibility, and unequivocal statement of test results, but not necessarily the most exact imitation of the practical use to which the material concerned is to be subjected. Tests of finished goods are not to be entirely avoided; but it must be remembered that the test deals not only with the material, but also with the construction. The separate influence of each of these factors is naturally not ascertainable. The effect is similar to that of one equation with two unknown quantities.

Even for tests of the material alone it is worth while first of all to develop an experimental procedure through systematic work. In order that the properties of the material may be most clearly indicated, it is necessary to determine the most practical shape for test samples and the most useful kind of test. The laboratories of the Staatliche Materialprüfungsamt at Berlin-Dahlem claim to be the first in Germany to have conducted thoroughly planned work on a large scale [1] and thereby to have prepared the foundation for the methods of physical testing of vulcanized rubber.

The knowledge so gained has stimulated numerous laboratories, not only in Germany but also in foreign countries, to extend the investigations. It has become possible to publish the conclusions which have been almost universally accepted by the rubber industry and its customers. The type and method of performance of the most useful physical tests have been offered as tentatively standard ones in a publication [2] of the Deutsche Verbandes für die

* Translated by E. F. Scheffler, E. O. Edelmann and N. A. Shepard.

[1] K. Memmler and A. Schob, "Beitrage zur Frage der mechanischen Weichgummiprüfung," *Mitt. Materialprüfungsamt, Berlin-Dahlem*, **27**, 174 (1909).

[2] **Richtlinien für die Prüfung von Kautschuk,** *der Technik*, **No. 76.**

Materialprüfungen der Technik. Thereby a very important first step has been made. In the statement of the quality of vulcanized rubber, use is made of universally recognized units of measurement, which are intelligible to workers in other fields.

The Investigation of the Elongation of Soft Rubber (Tension Tests)

The General Character of the Stress-Strain Diagram, and its Modification by Different Circumstances

If only the ultimate tensile strength and ultimate elongation are determined in elongating soft rubber, there are not sufficient data for judgment. The entire course of the elongation curve; that is, the corresponding relation between stress and strain, is of greatest importance.

It will be advisable at this point to discuss the general basis of the stress-strain diagram, concerning which considerable confusion is still often found to exist.

First attention will be given to "stress," which is the term generally used to signify the load per unit cross-section. In the case of elongation (and also of compression) reference is made to the cross-section which is perpendicular to the line of force. This cross-section changes with increasing elongation, being inversely proportional to the change in elongation if no volume change occurs simultaneously. Most compounds do exhibit a small change in volume, and therefore the proportionality is not strictly true. The relations are expressed by Poisson's ratio (*see* p. 396) which is understood to be constant over the entire range of deformation. In the course of a deformation, there are stresses not only proportional to the load but also inversely proportional to the instantaneous cross-section. The determination of this "true" stress is complicated and only difficultly possible even with the help of automatic recording devices. It has therefore become customary to refer the stress to the original cross-section; that is, the cross-section of the unstretched test piece. In the measurement of a part of a finished article the load may also satisfactorily be referred to the original cross-section.

Such difficulties are not encountered in determining elongation changes; i.e., "strain." Elongation is merely expressed as percentage of the original length.

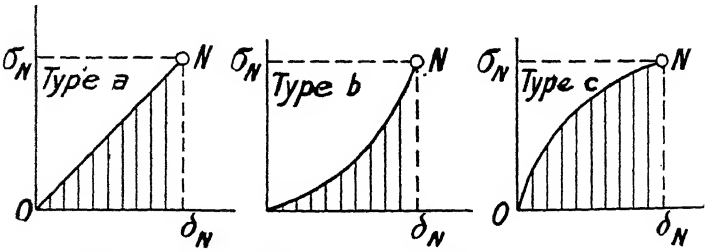


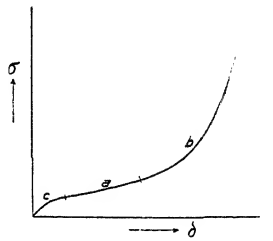
Figure 107 a-c—Principal types of stress-strain curves.

In the graphic representation, the elongations are ordinarily measured as abscissae and the stresses as ordinates. The stress is always considered to be the load divided by the cross-section of the original sample.

Consideration of Figure 107 a-c, which illustrates the principal types of stress-strain curves, shows how little the ultimate elongation and ultima

tensile strength indicate the characteristics of the material. The work (force × distance) which is performed to point N is shown by the area lying under the curve ON. N may be the breaking point or a suitable point on the stress-strain curve. In all three curves of Figure 107, the stress σn and elongation δn are of the same magnitude. Type *a* shows a strict proportionality between stress and strain; the work absorbed by the sample is $\frac{1}{2}\ \delta n\ \sigma n$. Type *b* shows less work than $\frac{1}{2}\ \delta n\ \sigma n$ and type *c* more than $\frac{1}{2}\ \delta n\ \sigma n$. If N is the breaking point, soft rubber of type *a* is unknown. Type *b*, always with an opposite curvature at the beginning, is most common; type *c*, often with an opposite curvature at the beginning, is less common.

Figure 108 [3] shows more exactly the characteristic stress-strain curve obtained upon the elongation of normal vulcanized rubber-sulfur mixtures containing pigments. In analyzing the stress-strain curve for soft rubber more closely, it may be considered as being composed of individual segments *c*, *a*, and *b*, corresponding to the types in Figure 107 a-c. By the addition of certain compounding ingredients, the upper portion of the curve in Figure 108 may approach a straight line upon further extension. A further portion of type *a* will follow type *b*, although at a greater angle to the abscissa; the lower segment of type *b* usually diminishes greatly.



ure 108—Normal stress-strain curve of vulcanized soft rubber containing no pigments.

As is apparent* from Figure 108, there is a point of inflection (that is, a point at which the tangent to the curve crosses the curve) in the normal stress-strain curve of soft, vulcanized rubber. This point of inflection has recently been studied by C. W. Shacklock [*Trans. Inst. Rubber Ind.*, **8**, 568 (1933)], who found it to be influenced by the cure, filler, and percentage of filler. The results of Shacklock indicate that the point of inflection cannot be eliminated from the curve by applying the correction suggested by Hatschek [*J. Soc. Chem. Ind.*, **40**, 251 T (1921)], and that the point of inflection must therefore be an inherent property of the curve. (Also *see* "Physics of Rubber," p. 395.)

The course of the stress-strain curve is dependent on various circumstances. The first of these involves the raw material; i. e., the crude rubber,[4] its botanical origin, the method of coagulation, and the conditions and length of storage before use.

Moreover even a first-class raw rubber can be injured by excessive milling during the mixing operation. In order for differences in the stress-strain curve to appear, it is not necessary that the rubber approach the "dead milled" state, since the results of tensile tests reveal even a slight overworking. Noticeable reductions in ultimate tensile strength and elongation are evident, provided there is material available for comparison which has been properly mixed. The comparison will, however, be inaccurate if the experiment is not planned specifically to study the influence of mixing.

[3] If a full treatment is to be presented at this point, it is impossible not to repeat certain material from the section on "Physics of Rubber" by Hock (even though Hock's discussion is mostly from a theoretical point of view).

* Translator's note by V. N. M.

[4] Consult the extensive work by O. de Vries in the various volumes of *Arch. Rubbercultuur.*

In this connection it may be mentioned that in almost all investigations of rubber there is a great factor of uncertainty, which can be sufficiently diminished only by careful laboratory technique.[5] Generally applicable directions can not be given here. The most satisfactory conditions for the actual circumstances must be determined so that they may be reproduced with certainty. The influence of conditions has been recently studied to a considerable extent, particularly in America, where systematic research was conducted at considerable expense after the war.*

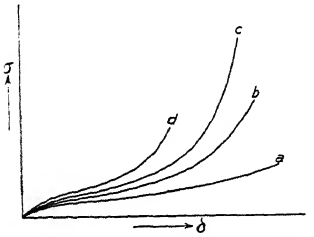


Figure 109—Influence of the degree of vulcanization the character of the stress-strain curve.

The influence of the degree of vulcanization on the character of the stress-strain curve is more easily grasped. The general characteristics of a rubber-sulfur mix without other compounding ingredients are illustrated in Figure 109. Four degrees of vulcanization, rising from *a* to *d*, are shown: *a* and *b* are undervulcanized (great elongation, low tensile strength); *c* is correctly vulcanized (maximum tensile strength, while maximum elongation is reached with definite undercures); *d* lies in the region of overvulcanization (great diminution in ultimate tensile strength and elongation). Within the rather narrow limits of the correct vulcanization, the values for ultimate tensile strength and elongation of individual tests are most constant. They are less constant in the region of undervulcanization (to the right of *c*), and least constant for overvulcanization (to the left of *c*). Overvulcanized rubber has, besides its rapid deterioration, an especially high susceptibility to tear in the case of a notched sample (*see* p. 601). It is possible for an increasing degree of vulcanization to change the curve from type *b* (Fig. 107 *b*) to type *c* (Fig. 107 *c*), with compounds containing a greater amount of pigments.[6]

If rubber is tested shortly after vulcanization and the tests are repeated at intervals, different values are obtained. In general, the physical properties improve upon resting several days after vulcanization. As an example, the results obtained with a slab prepared in the Materialprüfungsamt from 90 per cent Manihot rubber and 10 per cent sulfur are presented in Table 1.

TABLE 1.—*Effect of Time on Physical Properties of Vulcanized Rubber.*†

Time elapsed between vulcanization and testing	Ultimate tensile strength σ_z kg./sq. cm.	Ultimate elongation δ_z per cent
3 Hours	39.2	952
26 Hours	42.8	959
7 Days	54.4	992

† This is an undervulcanized sample, which type is influenced most extensively by a period of rest after vulcanization.

[5] See the dissertation for the doctor's degree by W. de Visser "Het Kalandereffect en het Krimpeffect van ongevulcaniseerde Rubber." (Amsterdam, 1925, J. H. de Bussy).

* Translator's Note. For details of work along this line, the reader is referred to *Ind. Eng. Chem.*, **17**, 535 (1925); *ibid.*, **20**, 1245 (1928); *India Rubber World*, **81**, No. 5, 7 (1930); and *Ind. Eng. Chem., Anal. Ed.*, 1 174 (1929). — E. F. S.

[6] The reference is still to the principal type the opposite curvature at the beginning of type b is naturally taken for granted.

Normally the testing is conducted seven days and at the earliest three days after vulcanization.[7]

Mechanical stress of any sort, if applied to the sample before the test proper, will have more or less of an influence on the test results, depending on the degree of stress.

Naturally the physical properties are dependent on the temperature to a considerable extent. Van Rossem and van der Meyden,[8] working with a rubber-sulfur mix, found the dependence of the stress-strain curve on the temperature to be as shown in Figure 110.[9] The influences of temperature and humidity have recently been thoroughly investigated by the United States Bureau of Standards.[10]

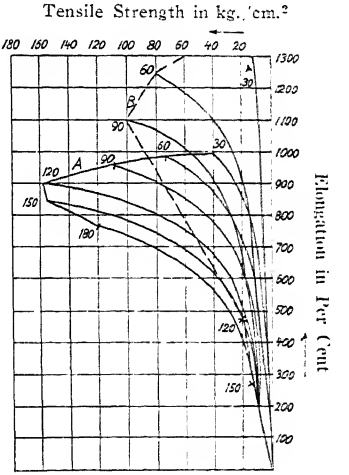


Figure 110—Tensile properties of first latex crepe at 13° C. (Group A) and at 147° C. (Group B), according to van Rossem and van der Meyden. (The figures at the ends of the individual curves indicate the time of vulcanization in minutes. The illustration should be turned 90° in a clockwise direction so that the coördinate axes correspond to the usual manner of presentation.)

The practical importance of the determination of tensile properties at 100° C. has recently been demonstrated by A. A. Somerville and W. F. Russell* [*Ind. Eng. Chem.*, **25**, 1096 (1933)], who made measurements on a large number of commercial inner tubes at 0°, 25° and 100° C. Some of these tubes were found to have very low properties at 100° C., whereas others exhibited tensile properties at 100° equal to or better than those at 25°. These investigators pointed out that the high-temperature test may reveal conditions of deterioration and overcure which are not noticeable in tests made at room temperature. The compounding and vulcanizing conditions which favor high tensile properties at 100° are discussed in the original article.

Compounding ingredients have a fundamental effect on the entire character of the stress-strain curve, depending on the specific materials and amounts used. The possible variations and combinations are so numerous that a mathematical analysis of the curves presents extraordinary difficulties.[11]

[7] The influence of conditions of storage after vulcanization upon the results has been recently thoroughly investigated. [*Ind. Eng. Chem.*, **20**, 1245 (1928)]. (Translator's Note. Laboratories in the United States generally perform tests 24 hours after vulcanization. E. F. S.)

[8] *Kautschuk*, **3**, 364 (1927).

[9] See also LeBlanc and Kröger, *Kolloid-Z.*, **37**, 205 (1925); and Tener, Kingsbury, and Holt, *Bur. Standards Tech. Paper*, **No. 364** (1928).

[10] *J. Franklin Inst.*, **206**, 385 (1928); Bur. of Standards, *Tech. Paper*, **364** (1928).

* Translator's note by V. N. M.

[11] P. Schidrowitz and H. A. Goldsbrough submit the equation of a conchoid curve for rubber. They cover only a very narrow field, however.

The breadth of the field and its consequent complexity are shown by the many curves for different mixes and degrees of vulcanization (*See* Fig. 111). Curves I-IV in Figure 111 are representative of four characteristic groups. Another source of difficulty is the insignificance of deviations within a group. In spite of their insignificance, these deviations frequently indicate pronounced differences which can be prominently shown by other tests. Thus many carbon blacks differentiate themselves in compounds only by the straight or slightly curved upper portion $x\ y$ of curve II in Figure 111, although crushing and elasticity tests show a marked difference. Even though the curves are not defined with mathematical exactitude, they may be limited to four principal types. The characteristic shapes of these can be remembered clearly and deviations quickly recognized.

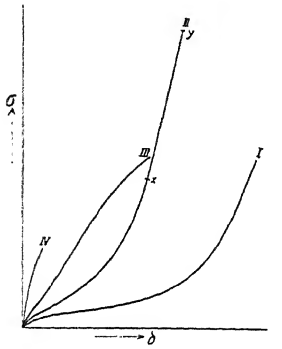


Figure 111—Stress-strain curves of typically different soft rubber compounds.

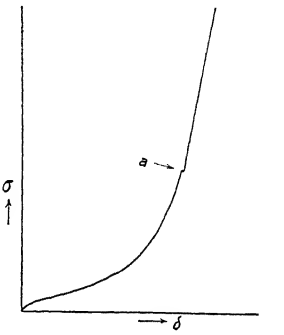


Figure 112—Tension test, with the progress of the elongation interrupted at .

There are conditions influencing the test results which are inherent in the test procedure. Those of importance are the shape of the sample (which is fully discussed in the next section) and the rapidity with which either the load is applied or the elongation made.* Undervulcanization postulates a greater susceptibility to the influence of speed than do normal or overvulcanization. For comparison of results, the speed must be standardized. For the usual technical testing, in which the speed is neither very fast nor very slow, it is not necessary to make special provisions to maintain a standard speed to within a few per cent. The effect of speed is not sufficiently great to require such standardization. Figure 112 illustrates the stress-strain curve of a rubber-sulfur mix with an ultimate tensile strength of 165 kg./sq. cm. (2346 lbs./sq. in.) and an ultimate elongation of 700 per cent. At point a (stress $\sigma = 76$ kg./sq. cm.; corresponding elongation $\delta = 570$ per cent) the machine was stopped, and the ring sample was allowed to rest for three minutes at the elongation of 570 per cent which had been reached. The load indicator was automatically held at the highest point, so that the actual drop in tension was not shown. Be-

* Translator's Note. A study of tensile tests at high speed has been made by A. van Rossem and H. B. Beverdam [*Rev. gen. caoutchouc*, **7**, No. 67, 27 (1930); *Rubber Chem. Tech.*, **4**, 147 (1931)]. They found that a ram pendulum is satisfactory for simple, high-speed tensile tests and for the direct determination of the optimum energy at rupture, but recommended that a better machine should be developed for more exact — V. N. M.

cause of the lowered tension in the sample, the curve runs horizontal for a short length upon starting the machine again. This length corresponds to an increase in elongation of about 12 per cent. Then follows an increase in tension, occurring with a smaller increase in elongation than was the case before stopping the progress of the test. This continues until the curve again coincides (after about 10 kg./sq. cm. [142 lbs. per sq. in.] increase in tension) with the extension of the curve below a. The disturbance at a is effective for only a small portion of the curve.

In concluding this discussion of the stress-strain curve, reference must be made to several points which are found in the American and English technical literature.

Schidrowitz [12] proposed the expression "slope" (or "type") to characterize a soft rubber. Slope is expressed in terms of the equation,

$$T = \frac{E_1 - E}{2.5}$$

in which E is the elongation at a load of 60 kg./sq. cm. (850 lbs./sq. in.) and E_1 is the elongation at a load of 104 kg./sq. cm. (1480 lbs./sq. in.). The choice of this portion of the curve is naturally arbitrary. The hypothesis that "slope" ("type") is characteristic for a certain rubber and independent of vulcanization or other circumstances is contradicted correctly by O. de Vries [13] on the basis of his numerous investigations of different rubbers. O. de Vries believes, however, that the upper portion of the stress-strain curve typifies certain properties of the material, and that a study of these relationships would be justified. He suggests the elongation at 130 kg./sq. cm. (1850 lbs./sq. in.) as a characteristic number, in addition to the ultimate tensile strength and ultimate elongation. This is based on his work, which has been mostly with rubber-sulfur mixes without other compounding ingredients, and which has had as its purpose the evaluation of rubber.

In the American rubber literature, the term "stiffness" is also used. It corresponds to the difference in stress which is necessary to raise the elongation of compounds without an accelerator from 600 to 800 per cent and those with an accelerator from 500 to 700 per cent. In the case of "slope" ("type") two stresses are fixed and the difference in elongation between them is the measure. With "stiffness" the reverse is true; two values for elongation are fixed and the corresponding difference in stress is the measure. The ultimate tensile strength and ultimate elongation alone do not give sufficient data for evaluation of the quality of soft rubber, as has been mentioned previously. The product of the ultimate tensile strength and the ultimate elongation, which is still often mentioned in the English and American literature as tensile product, shows still less. This product is a misleading quantity, since it does not show the character of the curve. (*Compare* with the discussion on p. 517 in connection with Fig. 107 *a-c*.)

"Slope" and "stiffness" convey an estimation of the character of the curve, although only to a limited extent. These quantities may be used if it is believed that the determination and reproduction of the entire curve is unnecessary. For thorough investigations, however, it is impossible to dispense with the complete stress-strain curve.

Finally, several remarks are in order with reference to averaging tests, as for Figure 107 *a-c* (*compare* the footnote on p. 533 also). The reasons for

[12] *India Rubber J.*, **51**, 505 (1916). [13] *J. Soc. Chem. Ind.*, **39**, 308T (1920).

the fluctuations of individual values for ultimate tensile strength and ultimate elongation are not clear if the curves are not plotted. It is uncertain whether they are caused by accident, small local effects, etc., or whether they are dependent upon characteristic inequalities in the properties of the material (particularly with respect to vulcanization), which are shown only by the complete diagram of each separate sample. In Figure 113 the values for the ultimate strengths and elongations are near each other. Considering these alone without reference to the entire curve[14] leads to the conclusion that the material is quite uniform. In Figure 114 the individual values are farther apart than in Figure 113, especially for the ultimate tensile strengths. They lie on the same stress-strain curve, however,

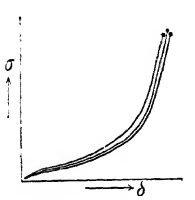


Figure 113—End points of different curves lying near each other.

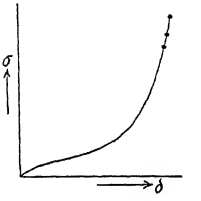


Figure 114—End points of identical curves showing divergence.

which indicates that the material is uniformly vulcanized. Great fluctuations are shown by the individual samples only when the curve reaches the higher portion. Material which has not been overvulcanized shows these differences principally because of accidental circumstances. Those of greatest importance are foreign bodies in the rubber and poor preparation of the samples, which lead to the latter being injured somewhat even before the test. With overvulcanized material, having no irregularities recognizable with the naked eye, these fluctuations are the rule. They are considered characteristic of the overvulcanized state. Such overvulcanized samples of soft rubber show a great susceptibility to tear after nicking, as has already been mentioned.

Before the discussion of test methods is continued, it must be understood that the preliminary treatment of materials, the temperature and speed of test, and other factors, the effects of which on the results of tension tests have been thoroughly discussed in this section, are of equal influence with respect to other sorts of stresses, such as pressure, bending or twisting; and the results will be affected in a degree corresponding to the particular test. In considering the remaining types of tests these topics will not be reviewed. However, they must be kept in mind.

Requirements with Respect to the Shape of Samples Used For Tensile Tests

In the matter of the requirements as regards the shape of samples for tensile tests, the following points can be mentioned:

[14] It is understood that the same units of elongation and tensile strength are used for each of the three curves. The elongations and loads should be read at suitable points by the "two observer" method and calculated to the proper units, and the curves drawn from these data. Another means is to make use of the automatic curve-drawing instrument of A. Schob, described on page 542. Instruments which are not adjustable cannot be used directly. Otherwise the unavoidable fluctuations in the measurements of the samples could create a condition as in Figure 113, although the individual curves are practically identical.

The samples must be simple, and the form must be reproducible with sufficient exactness. It must be possible to make clean cuts without difficulty (by using the proper tools) and thereby obtain samples which are affected as little as possible by minor influences and whose cross sections can be easily measured for the calculation of tensile strength.

Experience in testing materials in general has shown that test results are affected by the shape and size of the sample. Investigations in the Materialprüfungsamt have proved this to be true for soft rubber also. Therefore, a direct comparison of results obtained at different testing laboratories is only possible if a definite form of sample has been used in determining the data. For this reason the form to be used is so chosen that it can be made sufficiently uniform in practice and can be easily duplicated by all laboratories.

The sample must also be of such shape that it can be fastened without great difficulty in the machine used for tensile tests. Furthermore it must be so held in the machine that even with compounds of high elongation there will be no release at the grip. It is especially necessary that no further tightening by hand should be required during the test.

The ring-shaped sample has been adopted practically all over Germany as the usual test form for tensile tests on soft rubber (Fig. 126). In preparing the sample a closed ring is generally stamped out of a rubber slab. If the material to be tested is in tubular form, the test rings can be made by cutting the tube into sections perpendicular to its longitudinal axis. Besides the ring form, the rod-shaped sample is still used here and there.* These are prismatic in shape, with or without enlarged ends used for holding them in the grips, and are stamped out of a slab of rubber.

The use of rubber threads or rubber bands for tensile tests is also to be mentioned.

THE BAR-SHAPED OR DUMB-BELL TEST STRIP

Before the ring-shaped sample became the preferred type for tensile tests on soft rubber in Germany, samples in the shape of dumb-bells and bands were in use for this purpose almost universally. It was at this time that the Materialprüfungsamt began work on the mechanical testing of rubber. Their first efforts were directed to a basic study of the different bar-shaped test pieces. Although later German practice has developed overwhelmingly in favor of the ring test sample, an outline of the valuable data obtained from this study should be given here.

Memmler and Schob used six different compounds, in the form of slabs 6 mm. thick, for their investigation of the influence of shape of the sample on the results of tensile tests. In the choice of these compounds, particular care was taken that they should show characteristic differences in stress-strain properties, as found commercially.

The influence of shape was studied, using the six different types as illustrated in Figure 115. Four tests were run with each compound and with each test shape, both parallel with and perpendicular to the long dimension of the slab. Altogether 288 tests were conducted.

Samples of form A in Figure 115 were cut from the slab with an ordinary

* Translator's Note. It is general practice in America to use this type of test sample. (See discussion of "dumb-bell" test strips.) E.F.S.

knife. Samples of forms B and D were stamped out in a hydraulic press, using dies as shown in Figure 117.

The tensile tests were carried out with a Schopper-Dalen machine (described later). The grips illustrated in Figure 116 were used. The loads were increased at the same rate, and the corresponding elongations for the individual load increments were read from bench marks (10 and 30 mm. apart) previously placed on the sample. There were approximately 10 readings to the breaking point. Two different sets of bench marks were used to determine the effect on the elongation of length and of position with respect to the "dumb-bell" ends.

The extent to which the bar-shaped sample meets the requirements set forth above for a satisfactory form will be considered on the basis of the data obtained in this work.

The problem of easily making bar-shaped samples with sharp edges and plane surfaces would be overcome if the simple test strip A in Figure 115 could be generally applied. The data in Table 2, which gives the ultimate tensile strengths of the six compounds using the different shapes (each value represents the average of four individual tests), show that Form A

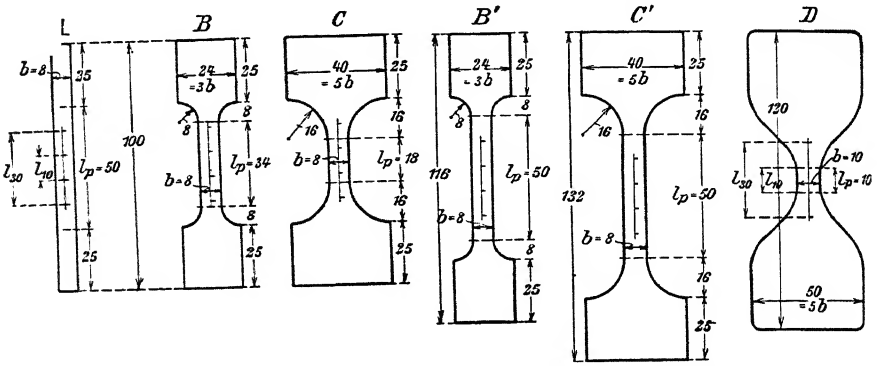


Figure 115—Various bar-shaped ("dumb-bell") samples.

is not generally applicable. This conclusion is drawn from the fact that, with most of the compounds tested, the ultimate tensile strength is considerably lower with Form A than with the other forms. Moreover, the results with the different compounds show a very wide variation in the values for the ratio of the tensile strength with Form A to the average tensile strength (*see* Table 2).

The pressure which is placed on the soft rubber sample by the grips of the testing machine influences the determination of the tensile strength to varying degrees. To overcome this effect, bar-shaped strips must have the ends broadened in proportion to the width of the strip itself. This necessity, which was previously observed in testing the tensile strength of flat bars of iron and steel, is generally recognized.[15] The types of these broader ends, as used in the testing of rubber, are shown in Figure 115, *B-D*. To attain the goal of straight cuts in making such samples from slabs is difficult. Rubber has the peculiarity of turning aside under the pressure of stamping; therefore the thicker the slabs the smaller is the

[15] See Martens, "Handbuch der Materialkunde für den Maschinebau," p. 41, section 71, J. Springer, Berlin, **1912.**

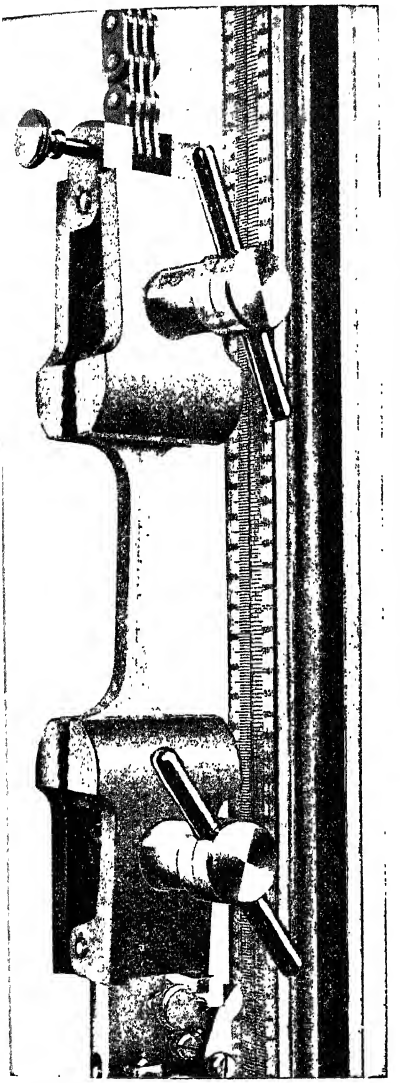


Figure 116 (left)—Clamps for bar-shaped samples.

Figure 117 (above)—Dies for bar-shaped samples.

possibility of getting a perfect cut. Contrivances described later (on p. 531), which are of value in making ring-formed samples, are scarcely worth consideration here, because of the great difference in profile between them and the dumb-bell strips. Moreover, in the case of soft rubber compounds it is very difficult to obtain altogether satisfactory samples with rectangular cross sections by vulcanizing in or grinding to the desired shape.

Besides the difficulties in making the test strips, there are those encountered in fastening them in the test machine. Because of the usually great deformation of soft rubber, the test pieces tend to slip from the

TABLE 2.—*The Influence of Different Bar Shapes on the Ultimate Tensile Strength of Rubber.*

Compound	Shape of sample (*See* Fig. 115)	First Direction of Sheet ∥ * Average ultimate tensile strength σ_z kg./cm.²	First Direction of Sheet ∥ * Ratio based on average = 100	Second Direction of Sheet ⊥ * Average ultimate tensile strength σ_z kg./cm.²	Second Direction of Sheet ⊥ * Ratio based on average = 100
I	A	16.2	29	17.6	30
	B′	43.2	78	46.2	78
	C′	—	—	—	—
	B	53.2	96	54.3	92
	C	77.6	140	91.6	155
	D	87.0	157	85.2	145
	Average	55.4	100	59.0	100
II	A	12.8	78	10.9	60
	B′	14.4	87	19.3	106
	C′	16.8	102	18.9	104
	B	16.8	102	22.3	123
	C	19.3	117	16.0	88
	D	18.9	114	21.6	119
	Average	16.5	100	18.2	100
IV	A	97.5	96	91.8	106
	B′	100.5	99	90.6	105
	C′	99.5	98	87.1	101
	B	114.5	113	92.5	107
	C	97.1	96	71.9	83
	D	101.1	100	84.3	98
	Average	101.7	100	86.4	100
V	A	30.2	48	36.4	55
	B′	52.4	83	76.5	116
	C′	68.7	109	63.3	96
	B	86.4	138	73.9	112
	C	66.1	105	65.7	100
	D	72.8	116	79.2	120
	Average	62.8	100	65.8	100
VI	A	16.5	60	12.5	67
	B′	29.5	108	20.1	108
	C′	29.5	108	19.9	107
	B	29.0	106	19.1	103
	C	30.7	112	19.8	106
	D	28.9	106	20.0	108
	Average	27.4	100	18.6	100
VII	A	16.2	75	16.4	80
	B′	23.5	109	20.6	100
	C′	22.6	105	19.9	97
	B	22.3	104	21.8	107
	C	22.2	103	23.3	119
	D	22.9	106	20.8	102
	Average	21.6	100	20.5	100

* The samples were taken from the sheets in two directions perpendicular to each other (lengthwise and crosswise).

grips before the break occurs in the free part of the sample, even when the grips have been very tightly fastened before the test. During the test the grips must be tightened. Repeated experiments have been made to prevent this slippage by increasing the friction between the sample and grips, harder rubber or fabric being used on the faces of the grips. Even

this expedient fails in most cases, when used on very extensible compounds of low pigment content. This further tightening of the grips during the test exerts an uncontrollable influence on the stressing of the sample. The difficulty of conducting the tests on a uniform basis is thus increased. Mechanical devices for increasing the pressure of the grips [16] are used to some extent, but they are uncertain in operation and often exert excessive pressure on the dumb-bell ends, thus causing a break at the grips instead of in the free portion of the test strip. Memmler and Schob found, during their research work with bar-shaped test pieces, that the additional stressing of the material caused by the fastening in the grips is very great in the case of compounds with great elongation, such as the one they used (tensile strength of 124 kg./sq. cm. [1763 lbs./sq. in.], and ultimate elongation of 828 per cent). With this compound, the breaks occurred in the broad ends of the strips (with one exception), regardless of the type of dumb-bell sample used. (*See* Fig. 115.) Since these breaks in the ends always started from the middle rather than the edge, a sample with even broader ends, that is, one having a ratio smaller than 1 to 5 between the length of the bar and the width of its ends, would not offer any greater assurance of success. Moreover, the difficulties of making such awkwardly shaped samples and of fastening them in the grips would be considerable.

The objections to the bar-shaped sample are not yet exhausted. To be able to ascertain the elongation at the desired points, the measurements must be made on the bar portion of the sample, because the characteristics of the fastening for this type of test (which are described above) allow no other method. Even for tests of but limited accuracy, the measurement of the elongation as the distance between the grips is impossible, because the slippage of the sample through the grips would introduce an error, varying in degree according to the compound used. Measurements of the elongation on the bar necessitates putting lines (bench marks) across the sample itself and determining the separation of these lines. Readings of both marks must be made during the test. Moreover, these readings of strain must be made simultaneously with those of stress, since the duration of the loading exerts a great influence on the elongation (as explained later). With original lengths of more than one centimeter this becomes difficult. Since it is necessary to avoid injury to the surface in making these marks, only ink may be used for this purpose. With increasing elongation, however, these marks become very broad so that the exactness of the measurements is decreased.

There are further practical difficulties with the bar-shaped sample, in that a ruler must be used to measure the elongation. For every reading the ruler itself or an auxiliary pointer must be brought to the marks by hand. If it were desired to fasten the ruler to the sample with suitable devices, as is usually done in tensile tests on metal, there would be no assurance that the instrument would not move, because the changes in cross section are very great in the case of rubber. Therefore, even in this case, the position of the ruler would have to be adjusted for each measurement of elongation. The determination of the ultimate elongation is difficult because the break may occur unexpectedly (particularly with very extensible compounds), and it is seldom that the elongation can be read

[16] *See* p. 547, Fig. 137A, where a device used by the United States Bureau of Standards is shown.

exactly at the instant of break. Several machines using bar-shaped rubber samples record the stress-strain curve automatically. The foregoing discussion arouses justifiable doubt concerning the reliability of such curves. Memmler and Schob [17] extended their investigations with the bar-shaped test pieces to include the extent to which the measured elongation is affected (1) by different distances between bench marks, *l*, and (2) by the ratio of the length *l* to the total length *lp* of the bar portion of the dumb-bell strip (*see* Fig. 115, p. 524). Since these values are known to have an influence in the testing of metals,[18] it seemed worth while to consider this question in testing soft rubber. The data showed that different lengths between bench marks (10 and 30 mm.) with shapes *A*, *B'* and *C'* (Fig. 115) had no influence on the measured elongation. With these three types of test strips, the distance between the bench marks is less than the total distance between the broadened ends of the strips, even when the bench marks are placed 30 mm. apart. Consequently the changes in cross section and length of the portion between the bench marks are not affected by the dumb-bell ends of the test strips.

These results are in direct contrast to those obtained in testing iron and other extensible metals, with which the size of the measured portion under observation (corresponding to the distance between bench marks) does influence the measurement of the elongation. In fact it is necessary to set up a certain initial relationship between the measured length under test and the cross section of the bar ($11.3\sqrt{F}$, rule of similarity; refer to the above mentioned literature reference), if comparable results are to be obtained. The explanation of this contrast lies in the fact that rubber exhibits an essentially different type of elongation with increasing load from that of iron or other metals (*see* p. 406). As a rule metals having a large change of form show a local constriction at the breaking point and the nearby vicinity, and this section has a greater specific elongation than the rest of the measured length under test. In order that the measured elongation shall not be influenced too greatly by this greater specific elongation near the point of break, it is necessary that the portion of the sample under test be rather long. With vulcanized soft rubber, the break occurs without any appreciable constriction, and there is therefore no necessity for a large distance between bench marks in order to minimize the effect of constriction at the point of break.

The tests conducted indicated that variation in the ratio of *l* to *lp* does not affect the measured elongation of bar-shaped samples, provided the measured length between the bench marks is kept within the limits of the free prismatic portion *lp* of the sample. Samples of Form D (Fig. 115), which were formerly used to some extent, do not comply with these requirements, since they have no prismatic portion whatever.

All of these conclusions indicate that the inexperienced worker can be easily led to incorrect conclusions regarding the properties and value of the tested rubber when using the dumb-bell strips. Therefore the use of this type of sample for testing soft rubber should be restricted to those cases where the ring-shaped sample cannot be used. The information which is necessary in connection with the use of the ring-shaped sample is given in the next section.

[17] *Mitt. Materialprüfungsamt, Berlin-Dahlem,* **27**, 173 (1909).

[18] See Martens, "Handbuch der Materialkunde für den Maschinebau," p. 94, section 141, J. Springer, Berlin, **1912.**

The bar-shaped* or dumb-bell test strip is in much greater favor in America than in Germany, and has been adopted as the standard form by the Physical Testing Committee, Rubber Division, American Chemical Society. This committee has published detailed recommendations regarding the following aspects of the preparation and physical testing of rubber samples: dimensions and temperature of the mill, mill opening, batch weight tolerances, mixing procedure, storage of mixed batches, preparation of raw stock for curing, curing, handling of molds, cooling of cured slabs, dieing of specimens, conditions for testing, measurement and marking of specimens, temperature and speed of testing, and evaluation of results. For details of this tentative laboratory procedure, the reader is referred to *Rubber Age (N. Y.)*, **26**, 429 (1930) or *Rubber Chem. Tech.*, **3**, 179 (1930). The standard procedure of the American Society of Testing Materials for the testing of dumb-bell strips is published in the "Book of A. S. T. M. Standards," section D 15-32, p. 1154 (1933), while that of the United States Government is described in U. S. Treasury Dept., Budget Bureau, Federal Standard Stock Catalogue, Section **14**, Part 5, ZZ-R-601 (1930).

THE RING-SHAPED SAMPLE

At least sixty years ago investigators were already using ring-shaped samples for tensile tests, probably to overcome the previously mentioned difficulties of fastening the bar-shaped samples. Stevart[19] used rings of 108 mm. outside diameter, without, however, stating how the rings were made. In the work of Breuil,[20] tests were conducted with ring-shaped samples, which were made from rubber tubing by cutting off sections of different widths perpendicular to the length.

The machine brought on the market in 1908 by Louis Schopper of Leipzig directed especial attention to the use of the ring-shaped sample for testing soft rubber. This machine will be thoroughly described on page 542. At the instance of Dalen (formerly on the staff of the Materialprüfungsamt), Schopper used ring-shaped samples. During the test, the rings move over rollers, which are part of a suitable contrivance fixed on the machine. In this manner, the entire length of the sample is uniformly elongated. There is a peculiarity in the use of these moving rings, the significant effect of which on the test results will be explained later. (*See* p. 537.)

In making ring-shaped samples, particular care must be exercised to obtain the most uniform rectangular cross section possible, in order that the area of the cross section for the calculation of the specific tensile strength of the material will be as free from objection as possible. There are three methods in use:

1. Vulcanization in the ring form.
2. Cutting from slabs.
   a. by stamping with a ring-shaped die.
   b. by a rotating knife (if the knife remains stationary and the slab rotates, the process is naturally the same).
3. Cutting of tubes.

The first method, vulcanization in the ring form, is not advisable. It is inconvenient, and the sample can easily be irregular. Moreover, there is the additional operation of removing the overflow.

With due regard to the dimensions of the particular soft rubber sample to be tested a choice is made between methods 2 and 3. Since stamping shows a considerable saving of time compared with cutting, an effort should be made to have the material for test of such dimensions that a standard die may be used. In those cases for which the standard die cannot be used methods 2b or 3 are employed.

* Translator's note by V. N. M.

[19] *Bull. musée ind. Belg.*, **57**, No. 5 (1870).

[20] *Caoutchouc & gutta-percha*, **1**, 54, 76 (1904).

Since deviations from the dimensions of the standard ring occur, particularly with respect to the cross section, the influence of different cross sections of the sample on the test results must be considered (*see* p. 534).

The method of stamping standard rings according to the procedure of A. Schob, using the Schopper stamping press for the purpose, is as follows:

From a slab 6 mm. thick, a disk 57 mm. in diameter is first stamped out, using the largest die. As shown in Figure 118, this disk is placed on a sheet of cardboard and properly centered in a conical centering ring, which is broadest at the bottom. A second die is used to stamp out a disk of 52.6 mm. which corresponds to the outside diameter of the standard ring. Using the same steps, but with a die 8 mm. less in diameter and a centering ring, another disk of 44.6 mm. is stamped out. Thereby the standard ring of 52.6 mm. outside diameter is completed.[21] If only a small amount of material is available, the process may be repeated, using a fourth die 8 mm. smaller and a centering ring to obtain the "small standard" ring of 44.6 mm. outer and 36.6 mm. inner diameter (for the justification for using the "small standard" ring without any correction, see the results of the investigation involving rings of different diameters, as given on p. 537). Neither water nor a soap solution is used for the stamping; the rubber is kept dry.

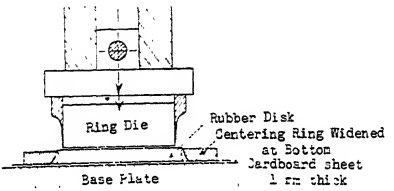


Figure 118—Preparation of ring samples by stamping.

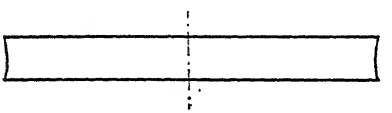


Figure 119—Concave cut (without centering ring).

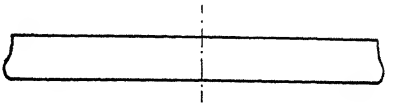


Figure 120—Convex cut (centering ring was too narrow).

The remaining disk of 44.6 mm. or 36.6 mm. diameter may be used for impact elasticity tests with the pendulum hammer (*see* p. 571). The large disk, which has a hole in the center, may be used for abrasion tests (*see* p. 594). A detailed description of the development of this stamping process has been given elsewhere by Memmler and Schob.[22] The necessity of the preliminary cut with the largest die and of the conical enlargement at the bottom of the centering ring are discussed in this article.

In stamping a round disk from a sheet of rubber the result is not a cylindrical cut because the die first presses the rubber together strongly before it actually cuts. Some of the material which is forced outward during the pressing springs back after the cut. Surfaces cut as shown in Figure 119 are the result. Even if the interior cut of the ring were cylindrical, an outer surface of such character would still be objectionable. Not only would the cross section measurement not be exact, but also the sharp edges would offer an opportunity for formation of nicks, which influence the results of tensile tests. If a disk of the shape shown in Figure 119 is mounted by means of a centering ring with no play, and a ring is cut in the manner illustrated in Figure 118, the shape of the resulting inside

[21] The inside diameter of 44.6 mm. is required by the rollers on the Schopper-Dalen machine; rings of 70 mm. inside semi-circumference are used as the standard sample.

[22] *Mitt. Materialprüfungsamt*, **27**, 178 (1909).

disk will be that of Figure 120. This is the case because the material outside the die is pressed inward before the cut takes place. Upon execution of the cutting, the material which has been pressed to the interior of the die springs back and an enlargement results. Therefore the centering ring which holds the disk must be broadened at the base so that the material which is pressed by the die will move neither inwards nor outwards. This enlargement of the centering ring can only be determined empirically. One ring for soft and another for harder compounds is sufficient, if the thickness does not deviate much from 6 mm.*

Figure 121 illustrates the usual stamping press for making test rings. The Schopper firm has also brought on the market another type of construction, in which the dies and centering rings are arranged on a revolving head (Fig. 122). This arrangement obviates the necessity for setting up and dismantling the apparatus for use with the various dies. Naturally, the dies are so equipped that the stamped-out disks can be readily removed.

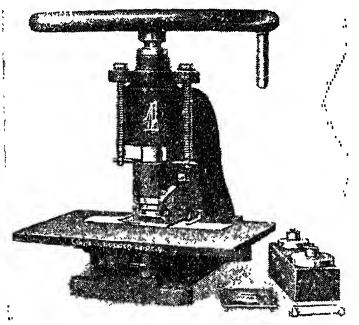


Figure 121 (Above)—Simple Schopper ring-punching machine.

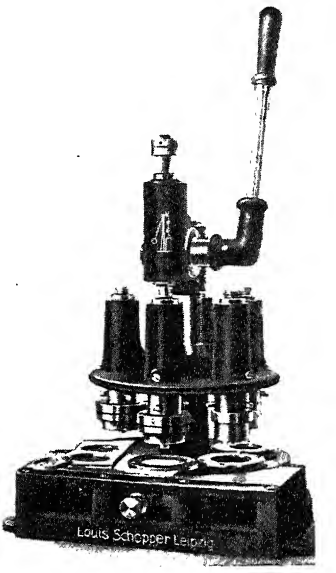


Figure 122 (Right)—Schopper ring-punching machine with revolving multiple cutter head.

If only rings and disks are required for testing the desired compounds, a suitable number of slabs (having a thickness of 6 mm.) are prepared, so that the number of samples necessary for duplicate tests can be obtained. Each ring necessitates a square with sides 60 mm. in length. If the compound is vulcanized in block form (so that, besides the rings and disks, balls for the crushing test described on p. 589 may be made) or if the rings are to be obtained from solid tires or similar articles, an octagonal block of 60 to 65 mm. diameter is cut, using a knife moistened with soapy

* Translator's Note. According to R. E. Lofton [*Ind. Eng. Chem., Anal. Ed.*, **4**, 439 (1932)], a microscope of low power may be used to advantage in measuring the cross-sectional dimensions of dumb-bell test specimens whenever an unusual degree of accuracy is desired. Lofton has observed that the width of specimens is usually greater than that of the die with which they were cut and that the thickness of soft compounds as determined by the microscope is greater than that indicated by a gage of the plunger type. — V. N. M.

water. The surface of one end is cut so as to be as smooth as possible, and then the block is mounted (by means of an adhesive) on a wooden cylinder. This cylinder is fastened in the chuck of a lathe. (Fig. 123.) Using a thin, pointed knife, which is kept moistened with soapy water or a dilute solution of soda, slabs of 6 mm. thickness are removed.

It is possible to make rings of other than standard dimensions by stamping provided they are not too thick nor too small. If certain other sizes are encountered frequently, a suitable set of dies and centering rings should be provided. Otherwise, samples must be cut on a lathe as shown in Figure 124 (which illustration is self-explanatory). To obviate gluing the disk of rubber, a wooden cylinder, cardboard sheet, and the rubber are loosely laid together and held by the tail stock spindle. If clean-cut rings are to be obtained, however, it is often necessary to fasten the rubber disk directly to the wood with an adhesive. The pressure of the tail stock spindle is not then required.

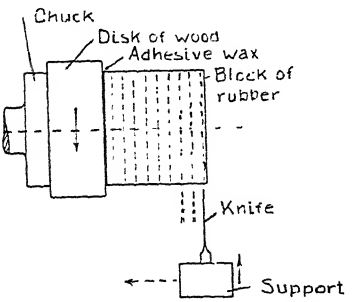


Figure 123—Cutting of disks 6 mm. thick on a lathe.

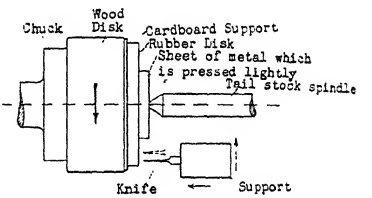


Figure 124—Preparation of ring samples by cutting on a lathe.

The cutting of rings from tubing is carried out essentially as illustrated in Figure 123, except that, instead of the block of rubber fastened to the disk of wood, a wooden mandrel is fastened directly in the chuck. The tail stock is used as a support only in the case of longer mandrels. The diameter of the mandrel should be so chosen that the tubing is not stretched greatly while being pulled into place. On the other hand, the tubing should be so tight that it does not turn during cutting or grinding. (Grinding is occasionally required to smooth the outer surface before cutting the rings.)

To test the ring-shaped sample, Memmler and Schob used the same six compounds which were used in their investigation of the bar-shaped sample. Rings of 52.6 mm. outer diameter and 44.6 mm. inner diameter (and with cross sections of 4x6 mm.) were subjected to tensile tests on the Schopper machine. The results of these tests on the rings led to conclusions which will be considered briefly.

1. As has been mentioned, rings for test purposes can be made easily and with sufficient exactness. Therefore it is possible to make test pieces freer from objection with the ring-shaped form than with the dumb-bell shape.

2. The fastening of the ring in the tensile test machine, the procedure of the test itself (*see* p. 542), and the method of measuring the elongation

are all considerably simpler and more reliable procedures than is the case with the dumb-bell strip. (*See* p. 527.) The ring test on the Schopper machine requires no further attention after adjustment of the sample and starting the machine.

3. In contrast to the bar test, the ring test may be used with soft rubber compounds having very great elongations. Dumb-bell strips are denied this application because the breaks occur in the grips, and consequently the results are not free from error.

4. If the load on strips and rings of the same compound is increased by steps, and the corresponding elongations are plotted on stress-strain curves (as has been done in Figure 125), the curves of all six compounds in the strip form lie to the left of those tested in the ring form. Therefore, for the same load, strips give a smaller elongation than ring samples.[23]

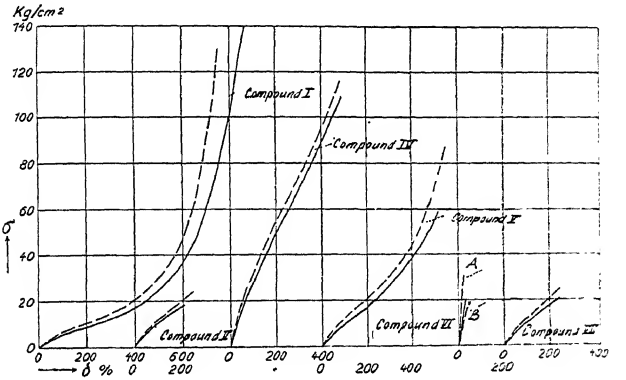


Figure 125—Stress-strain curves of different soft rubber compounds determined with ring- and bar-shaped samples.

A—First direction of sheet —Ring samples.
B—Second direction of sheet · Bar samples.

One objection to the ring-shaped sample is the impossibility of determining differences in tensile strength and elongation parallel and at right angles to the length of the slab. If it is only required to find the direction of lowest tensile strength, this is easily accomplished by drawing a line on the slab (parallel to the length, for instance) before stamping out the rings. From the position of the break with reference to the mark, the direction of least resistance is found. Naturally the average of several tests is taken, since the break occurs at the weakest point, and the location of this point is dependent on certain variables such as non-uniformity in the grain of the rubber or in the compounding ingredients. Therefore, several tests are necessary to determine to what extent the results are due to chance and to rule respectively.[24]

[23] Similar investigations by the Bureau of Standards gave the same results, as is shown in Circular No. 38 of the Bureau (5th ed., 1927).

[24] The esteemed rubber investigator, Dr. K. Gottlob, who unfortunately died too soon, held that only those results which showed the highest tensile strengths should be chosen from a set of tests. All the lower values are caused by disturbances which have nothing to do with the material. In some instances this view is allowable; for example, when the study is concerned solely with the effect of a compounding ingredient. This method is not suitable for the practical examination of a compound, however. To insure a greater factor of safety, it would be better to use the smallest values. It is not necessary, however, to apply this extreme. As is the general practice, the average values are used, and when the individual values deviate greatly from the average, these deviations are also given.

If it is desired to examine the tensile and elongation properties more closely in a certain direction—for instance, if an investigation of the so-called calender effect is undertaken—there is no alternative but to use the strips, in spite of their deficiencies. The results of the investigations by Memmler and Schob showed the extent of these deficiencies, and how they prevent proper evaluation of a rubber-sulfur mix with respect to ultimate tensile strength and elongation. Testing such a compound in the dumb-bell strip form (consequently not Form A, Fig. 115) showed an ultimate tensile strength of 67 kg./sq. cm. (953 lbs./sq. in.) and an elongation of 654 per cent. Using the ring-shaped sample on the same compound, they obtained an average of 124 kg./sq. cm. (1763 lbs./sq. in.) for the ultimate tensile strength and 828 per cent for the average elongation at break. This example shows the great influence which the choice of the form of sample can have on the results of tensile tests made on rubber. It is worth while to weigh carefully the advantages and disadvantages of the test forms before the decision is made in favor of a particular one.

Investigations had to be carried out to determine the nature and extent of secondary influences in the case of ring samples.

In the first place, it was necessary to determine what effect the dimensions of the ring would have on the test results, and what dimensions would be the most suitable. Memmler and Schob used four different compounds; namely, samples I, II, Va and VIIa which had been used in the earlier work, (the last two were from a later supply of V and VII). Tests were carried out with rings of different dimensions on the Schopper-Dalén machine. The equipment for stamping out the rings and procedure for testing described on p. 531 were used.

In order to study the influence of variations in width (b)[25] of the ring on test results, rings having widths of 2, 4 and 6 mm. and the same inside diameter were stamped out of the same compound. The necessary dies and corresponding centering rings for cutting the outside diameter were made especially for this test. It was found that rings 4 mm. wide, such as were used exclusively in the first investigations, were of the size which could most easily be made to exact and uniform dimensions. In spite of very close fitting centering rings, wide samples make it difficult to obtain a cylindrical cut with soft compounds. With very small rings, on the other hand, the outer surface easily becomes concave. The space between the disk and the centering ring must be very accurate, and the centering becomes difficult and uncertain. Moreover, small differences in the hardness of compounds and small differences in the thicknesses of slabs unfavorably influence the possibility of obtaining good cylindrical rings.

The results of these tests are tabulated in Table 3. The values σ_z and δ_z for each width represent the averages of 15 separate tests, 180 tests in all being run for this purpose. According to these results, the tensile strength of extensible compounds decreases as the width of the ring increases. In contrast with this, the ultimate elongation is not appreciably influenced by the width of the ring. Logically, widths (of the ring) sufficiently greater and smaller to determine whether the curves for the ultimate tensile strengths finally become asymptotic to one of the coördinate axes should have been used. Difficulties in performing the test prevented this, however. It is impossible to prevent tipping on the rollers as the load increases, if the ring has a greater

[25] *See* Fig. 126. The terms "width" and "thickness" of the ring are not used as is customary, since "width" refers to the thickness of the slab from which the rings are taken.

TABLE 3.—*Comparison of the Results for Tensile Strength and Elongation when using Rings of Different Widths. (2, 4, 6 mm.)*

Compound	Width of ring b mm.	Ultimate tensile strength σ_s kg./cm.^{2}	Ultimate elongation δ_s per cent	Ratios (4 mm. width = 100) for σ_s	Ratios (4 mm. width = 100) for δ_s
I	2	158.9	808	135	100
	4	117.7	806	100	100
	6	97.4	809	83	100
II	2	18.9	182	101	94
	4	18.8	193	100	100
	6	17.2	183	91	95
Va	2	105.8	611	109	99
	4	97.1	624	100	100
	6	87.5	628	90	101
VIIa	2	25.2	187	92	93
	4	27.3	202	100	100
	6	26.0	199	95	99

width than thickness. Even with the square cross section (6 mm. width, 6 mm. thickness), a tendency to tipping begins to be disturbing with the more extensible compounds.

Rings of widths less than 2 mm. can not be stamped out with sufficient exactness, as explained above. Smaller rings can be made by circular cutting, as described on p. 532 (*see* Fig. 124), should this become necessary for any reason.

If slabs of greater or smaller thickness are used instead of those employed in these investigations, other widths may be used. However, little deviation from the ratio 2 to 3 (2 = width, 3 = thickness; Fig. 126) is permissible, because of practical difficulties, as previously mentioned. A change in the ratio in one way causes tipping on the rollers; a change in the other direction causes difficulties in stamping out accurate rings.

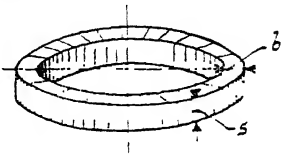


Figure 126—b = width of ring.
s = thickness of ring.

For testing out different thicknesses for rings, or rather, different thicknesses of the slabs from which the rings are made, it was necessary to use the same materials as were used in the preceding tests, in order that differences in vulcanization would not affect the conclusions. The largest permissible thickness was one of 6 mm.

Breuil[26] conducted similar tests with rings of different thicknesses. He cut different widths from rubber tubing (8, 10, 20, 29, 40 and 60 mm.) perpendicular to the longitudinal axis. Following the procedure of Stévart,[27] he put the rings on hooks which were used for grips on a three-ton testing machine, and determined the loads corresponding to certain elongations measured between marks on the rings. Breuil concluded that the loads per sq. mm. for similar elongations are practically the same for different "widths" (thickness s in Fig. 126). Only the "widths" of 40 and 60 mm. gave smaller values for ultimate tensile strength.

[26] *Caoutchouc & gutta-percha*, **3**, 56 (1904). [27] *Bull. musée ind. Belg.*, **57**, No. 5 (1870).

For the tests of Memmler and Schob, disks of different thicknesses, *a* and *b*, were cut from 6 mm. slabs, the cuts running parallel to the surface of the slab. This operation was carried out on a lathe, using a thin knife, very much as shown in Figure 123. Rings were then made from these disks, using the method illustrated in Figure 124. This investigation was confined to three very different compounds; namely, I, V and VII, which had been used in previous work. They are marked I to III respectively in Figure 128. Ten tests were run for each different ring dimension, using each material. With a constant width of 1 mm. and inside diameter of 44.6 mm. the thicknesses used were 1, 2, 3, 4, 5 and 6 mm. Furthermore, with a constant thickness of 6 mm. (except for deviations in the thickness of the original slab) different widths, 1, 2, 3, 4, 5 and 6 mm., were used (also with an inside diameter of 44.6 mm.). Since a disk of the thickness of the 6 mm. slab was cut into two parts,

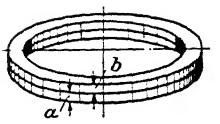


Figure 127

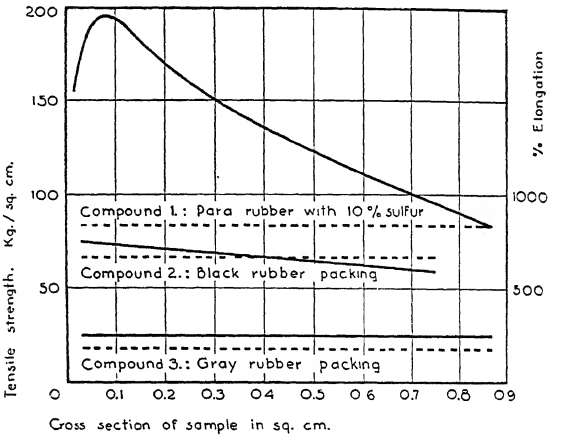


Figure 128—Tensile tests using rings of different cross sections.
———— Ultimate tensile strength
- - - - - - - - Ultimate elongation
Dependence of ultimate tensile strength and ultimate elongation on size of cross section.

a and *b* (as in Fig. 127), to make rings of 1 to 5 mm. thickness, only one part, *a*, for example, could be cut to the exact dimension. The other portion deviated by one to several tenths of a millimeter from the desired dimension, since the slabs were not exactly 6 mm. in thickness. To cut this second part to an exact dimension involved practical difficulties and was not attempted, since the amount to be removed was usually only a few tenths of a millimeter. Grinding was also rejected, because this process gives a rough surface, which would undoubtedly start tearing (because of small nicks) so that the results would be subject to an influence beyond control.

The remaining portions of the slabs, which had a diameter of 44.6 mm., were used for further study of the effect of different inside diameters of the ring. Rings were made with a thickness of 6 mm. and widths of 1 to 5 mm. Their outer diameters had the constant value of 44.6 mm., whereas their inner diameters were 42.6, 40.6, 38.6, and 34.6 mm. respectively.

The rate of loading was held as constant as possible with individual materials, as should be done in all comparative tests on soft rubber. The time interval between making the rings and conducting the tests was also kept constant, to avoid the possibility of different degrees of aging. It was necessary to stretch those rings with diameters less than 44.6 mm. a little to put them on the rollers, since the rollers on the Schopper-Dalén machine are set for rings with an inside diameter of 44.6 mm. Since only the ultimate tensile strengths and ultimate elongations were determined, this small stretching had no effect on the results (*see* p. 520, Fig. 112). The shape of the cross section seemed to have no appreciable effect, at least in the range of varying thicknesses and widths chosen. Therefore, the results of these tests have only been presented in a form which illustrates the dependence of ultimate tensile strength and ultimate elongation on the size of the cross section. The curves in Figure 128, which were drawn through the numerous, rather scattered points representing the individual tests, show the results. Only the ultimate tensile strength seems to be affected by the dimensions of the ring. The curves for the ultimate elongations of all three compounds are straight lines parallel to the horizontal axis.[28] A positive effect of the size of the cross section on the ultimate tensile strength is evident only with Compound I, which had a great elongation. The tensile strength decreases with increasing cross section, starting at about 0.1 sq. cm. This decrease in tensile strength is also noticeable with Compound II, but the extent is very much less. Compound III, which has a low elongation, does not show an appreciable effect. With cross sections less than 0.1 sq. cm., Compound I gives a decrease in tensile strength with a decrease in cross section. Samples with small cross sections show marked scattering of individual values. Doubtless accidental influences are chiefly responsible. The smaller the cross section, the greater is the effect of flaws in the compound (or non-uniformities of any kind) on test results.

The fact that the ultimate tensile strengths of the more extensible compounds are appreciably influenced by the dimensions of the samples, while the ultimate elongations are unaffected, leads one to surmise that the tension in the outer surface of the ring plays an important part. The effect of this tension increases as the elongation of the compound increases.

To ascertain the influences which different inside diameters of rings exert on tensile strength and elongation, the average results for 10 samples, having the same cross section but different inside diameters, are compared in Table 4. (These are the same compounds as in Fig. 128.) The column headed "Ratios" gives the figures for ultimate tensile strength σ_z and ultimate elongations δ_z for rings having an inside diameter less than 44.6 mm., when the corresponding values of rings with an inside diameter of 44.6 cm. are set at 100. No definite effect of the size of the inside diameter on the ultimate tensile strength and elongation is apparent from these tests.

As mentioned previously, the Schopper-Dalén machine is especially characterized by the fact that the rings do not remain stationary on the rollers during the test. By means of a contrivance which will be described later in the general description of the machine, the rings continually move over the rollers so that they are elongated uniformly over their entire circumference. Without this movement of the ring, that part which rests on the rollers would not have the same changes in cross section or in elongation as the free portion of the ring between the rollers. Since the free portions suffer a very

[28] In this connection, compare Breuil's results.

4.- *The Effect of Different Inside Diameters of the Ring Sample on Tensile Strength and Elongation Data.*

Compound	Ring: Thickness mm.	Ring: Width mm.	Inside diameter of ring mm.	Ultimate tensile strength σ_z kg./cm.²	Ultimate elongation δ_z %	Inside diameter of ring mm.	Ultimate tensile strength σ_z kg./cm.²	Ultimate elongation δ_z %	Ratios (with rings having inside diameter of 44.6 mm. = 100): σ_z	Ratios: δ_z
I	1.0	6.7	42.4	175	844	44.4	171	838	102	101
	2.0	6.7	40.6	143	823	44.7	147	817	97	101
	3.1	6.7	38.5	126	838	44.6	138	843	91	100
	4.0	6.7	36.6	116	854	44.7	119	842	98	102
	5.0	6.7	34.4	99.8	852	44.5	108	842	93	101
II	1.1	5.9	42.3	60.5	604	44.5	61.2	602	99	100
	2.0	5.7	40.6	65.6	630	44.6	56.5	578	116	109
	3.0	5.7	38.4	63.9	655	44.6	67.9	658	94	99
	4.0	5.7	36.6	57.8	628	44.6	58.3	618	99	102
	5.0	5.7	34.5	45.7	607	44.5	47.8	576	95	105
III	1.0	6.5	42.6	25.7	188	44.7	23.2	176	111	107
	2.0	6.5	40.7	26.0	192	44.7	26.4	193	99	100
	3.0	6.5	38.3	25.3	192	44.5	24.9	187	101	103
	4.1	6.4	36.4	27.3	202	44.4	27.0	197	101	104
	5.1	6.5	34.5	25.8	203	44.7	25.4	194	102	105

marked reduction in cross section, the parts on the rollers seem to become enlarged during the test, in the case of stationary rings. Tests performed by Memmler and Schob in comparing moving and stationary rings appear interesting. These were conducted with rings 4 mm. wide, made of four different compounds. The results of these tests are tabulated in Tables 5 and 6. Only the averages of 15 individual tests are shown.

When the rings remain stationary during the tests, there is a great effect on the test results, as shown in Table 5.

TABLE 5.—*Comparison of the Ultimate Tensile Strengths of Stationary and Moving Rings.*

(Width of ring $b = 4$ mm.)

Compound	Method of Test m = moving ring st = stationary ring	Ultimate Tensile strength σ_2 kg./sq. cm.	Ratios (moving rings set at 100)
Ia	m	117.7	100
	st	60.4	51
IIa	m	90.8	100
	st	21.5	24
Va	m	97.1	100
	st	56.0	58
VIIa	m	27.3	100
	st	24.7	91

The ultimate tensile strength of compound IIa is reduced 76 per cent. Different types of compounds, however, are affected to different degrees when the rings made from them are kept stationary (9 to 76 per cent reduction). The investigations of Stévart and of Breuil with rings (*see* p. 529) must have been subject to this effect also, since the rings were stationary. The extent

to which their conclusions concerning ultimate tensile strength are valid must be judged with the foregoing in mind.

It was more difficult to make a direct comparison between the elongations with stationary and with moving rings. With the latter, the elongation is measured directly, as the increase of the inside diameter of the ring. As previously mentioned, this is done by a special device which is part of the machine. For stationary rings, this method of measurement of elongation does not give satisfactory results, as can be readily perceived. The part of the ring in contact with the roller is not elongated to the same extent as the free part of the ring, because of friction between ring and roller. Therefore, the distance between the rollers does not give the correct value for the elongation. In addition to the automatic measurement on the Schopper-Dalén machine, Memmler and Schob also measured the increasing distance between two marks on the inside circumference of the ring. These were originally 20 mm. apart. This is similar to the method of measurement of elongation used by Stévart and to that employed when dumb-bell samples are used. The results of these measurements are presented in Table 6. The figures are averages of 15 individual tests.

TABLE 6.—*Comparison of Elongations Obtained in Different Ways on Stationary Rings.*

	Measurement of Elongation		
Compound	Using marks δ %	Using device on the Schopper machine δ_1 %	Ratio ($\delta = 100$) for δ_1
Ia	703	656	93
IIa	532	465	87
Va	501	460	92
VIIa	169	142	84

The ratios in this table show what effect the method of measurement has upon the results. Naturally, the difficulty of reading from both marks simultaneously, and the widening of the marks experienced with dumb-bell samples (*see* p. 527) also are encountered when marks are used on rings.

Considerable criticism has been made of the ring-shaped sample, particularly by the United States Bureau of Standards in its Circular No. 38. This criticism in no way challenges basic principles, however. The impossibility of using the ring test piece for those cases requiring stress-strain data in a particular direction, as in the study of the so-called "calender-effect," has been mentioned on p. 533. The objections of the Bureau of Standards on this point are incontrovertible.

The chief objection to the ring test is the variability of tension (and consequently of elongation) in the cross section. This is unavoidable, because of the difference in inside and outside diameters. In Circular No. 38 (Bureau of Standards) the calculated difference in tension between hypothetical threads in the inner and outer circumferences of the ring is given as 17 per cent. Actual tests show that this effect becomes less as the percentage of filling material increases. Compounds having high physical properties are consequently subject to this influence. The experience of the Materialprüfungsamt has been that these same compounds, when tested in the form of dumb-bell strips, give the greatest difficulty in fastening in the grips. The decrease in tension between the inner and outer layers of the ring also affects the measurement of the elongation. The elongation is taken from the inside circumference of the ring. This explains why the curves for the ring lie to

the right of those for the dumb-bell samples in Figure 125. The investigations made at the Bureau of Standards yielded similar results.

The significance of this variation of tension and elongation in the ring sample should not be overestimated. Table 4 shows that within the limits chosen there is no regular effect caused by the size of the inside diameter. The figures in the column headed "ratios" show no regularity. Accidental variations outweigh any possible effect. This table, however, does definitely show another influence acting in a regular manner; namely, the effect of the cross-sectional area on the ultimate tensile strength (the ultimate elongation is unaffected). The position of the stress-strain curve is, therefore, dependent on the cross-sectional area. This indicates that there is a strong element of relativity in tensile tests of soft rubber. Therefore, the much repeated assertion that bar-shaped samples should be used to obtain the "true" tensile strength of soft rubber becomes meaningless, because there is no such thing as a "true" value, even when the factor of time is left out of consideration.

All of these tests and discussions show that in general the ring sample is preferable to the bar-shaped sample for tension tests on soft rubber. The latter may not be entirely dispensed with, particularly in those instances when it is not possible to make rings from the samples available for testing. A standard method for the preparation of the rings, as well as standard dimensions for them, had to be set up, because both the dimensions and preparation of samples influence the test results. By such standardization, it has become possible to compare directly test results obtained in different laboratories. The committee for the testing of rubber of the "Deutsche Verbande für die Materialprüfungen der Technik" has decided on the following standards with reference to ring samples for tension tests on soft rubber:

Test Samples:

(A) Rings:
- (1) Large standard rings, 52.6 mm. outer, 44.6 mm. inner diameter; 6 mm. thickness.
- (2) Small standard rings, 44.6 mm. outer, 36.6 mm. inner diameter; 6 mm. thickness (made of the disks left from the large standard rings).
- (3) Rings of other dimensions, when standard rings are not possible.

(B) Other test forms (bars, strips, bands, or threads) whenever it is impossible to make rings.

Preparation of the Sample:

A (1) and A (2). Large and small rings are stamped from slabs, using the Schopper die. Cutting with a curved knife or on a lathe is permissible. Samples vulcanized in the ring form may be used, if they have a right-angled cross section, and are of the above standard dimensions. If slabs of 6 mm. thickness are not available, they are sliced from large pieces on the lathe. In certain cases, standard rings may also be cut from tubes by the method mentioned for A (3) below.

A (3). Rings of different dimensions (from tubing, for example) are cut on a lathe, after the tubing has been pulled on a wooden mandrel. If the tubing has variations in thickness of the wall or if the wall is too thick, it can be ground down on a rapidly revolving emery or carborundum wheel.

The rings are cut to a 6 mm. width, corresponding to the 6 mm. thickness o standard rings.

Under exceptional circumstances such that rings cannot be made from th material submitted for test, or when the special purpose of the test require it, samples in the form of bars, strips, or bands may be used. Under suc conditions the dimensions are governed by those of the material submitted. I is advisable to use a cross section as near that of the standard ring as possible

Bands and Tapes

Rubber bands and tapes, which are manufactured in a large variety o forms for numerous uses, cannot readily be subjected to tension tests in an other than their original forms.

If a portion of a band or a piece of tape were cut and fastened in the usua clamps for physical testing, the bar-shaped form without a head (Form A Fig. 115) would result. This form has been shown to give misleading results with compounds having high values for tensile strength. Even with compounds containing a high proportion of filling material, great care must be taken in fastening the sample in the grips. In practice rubber bands and tapes are sometimes tested by wrapping the ends around a cylinder and then applying tension. This type of fastening has undoubted advantages over the use of clamps. There still remains an uncontrollable effect such as experienced with stationary rings on rubber compounds of high quality. The portion in contact with the cylinder is prevented from undergoing the same change in form as the free portion. Therefore, there is an abrupt change in the cross-sectional area between these two portions.

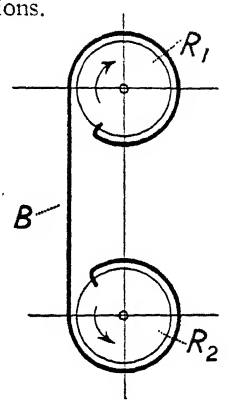


Figure 129—Schob's method of testing rubber bands and threads.

In order to have the same test conditions for bands and tapes as for moving rings, A. Schob has suggested fastening the sample on cylinders which are not caused to separate from each other but which stretch the sample by progressively winding it up. In that way, abrupt changes in the cross-sectional area are eliminated. Figure 129 illustrates this scheme. The rubber band B is wound on the rollers R_1 and R_2 which turn in opposite directions. R_1 and R_2 have the same diameters. To prevent the sample from winding up on itself they are threaded (screw threads). The tensile strength is measured as the moment of rotation by spiral springs on the axes of the rollers. The elongation is also obtained mechanically from the number of revolutions by making use of an empirically determined factor. The apparatus is built by L. Schopper.

Machines for Determining Stress-Strain Characteristics of Soft Rubber

Schopper-Dalén

The introduction over twenty years ago of the ring-shaped sample for testing rubber was greatly simplified by the fact that in the Schopper-Dalén machine there already existed a suitable apparatus for testing these rings. The first model, which was designed for a maximum load of 100 kg., is not satisfactory for present-day compounds, since these have considerably greater tensile strengths than can be measured by such a machine. Models with a maximum loading capacity of 250 kg. have been built for several years by the Schopper organization. One of these more recent models is shown in Figure 130.

The rubber ring is placed on the rollers R_o and R_u. The upper roller R_o is attached to a dynamometer which acts as a pendulum balance. R_o turns freely on ball bearings. The bottom roller R_u is attached to a support K_2 which is moved up and down by the screw L and the pulley A. Parallel to L is a rack (difficult to identify in Fig. 130) fastened to the frame of the machine. A pinion adjacent to the support of the lower roller R_u fits into the rack and drives R_u. In this manner, the lower roller is constantly turned as the support K_2 is moved up or down. The test ring conveys the motion to the upper roller R_o. The sample moves over the rollers while its length changes, thereby attaining a uniform elongation on the entire circumference.

The tension exerted on the ring sample is shown on the scale K_r by the deflection of the lever H. If the weight G is removed from the lever, the greatest deflection of the lever corresponds to the tension of 100 kg. This allows a greater degree of accuracy in reading small tensile strengths.

Since the rubber ring is uniformly elongated by its movement over the rollers, the elongation is shown directly by the distance between the rollers R_o and R_u and may be read on the endless measuring tape D. At break, the lever H and the tape D remain at the highest values reached. The subjective determination of the elongation at break at the instant of break by means of a ruler held against the sample (as is necessary with bar-shaped samples) is thus avoided. An autographic recorder *Sch* of simple construction is attached to record the progress of the test (reciprocal relation between the load and elongation of the sample).

The newer machines of this construction are driven either by belt, connecting gear, or separate electric motor. The older machines often were built for hydraulic drive by water pressure.

By exchanging the rollers for other appropriate means of holding samples, the machine can be arranged for tension tests on bar-shaped samples, and also for compression and bending tests.

These Schopper machines are also fitted with the autographic recorder of A. Schob.[29] This recorder differs from the usual ones in that the units for the coördinates can be varied. The recorded value for the force with the Schopper machine is proportional to the sine of the angle α (Fig. 131) which the lever H forms with the vertical. The recorded value, therefore, has the magnitude of $r \sin \alpha$. By setting r inversely proportional to the original cross sections of the different samples on the arm L, the ratio of the actual motion of the machine to the motion of the recording device is varied in such a manner that the readings are not influenced by the size of the cross sections.

[29] *Gummi-Ztg.*, **37**, 235 (1923).

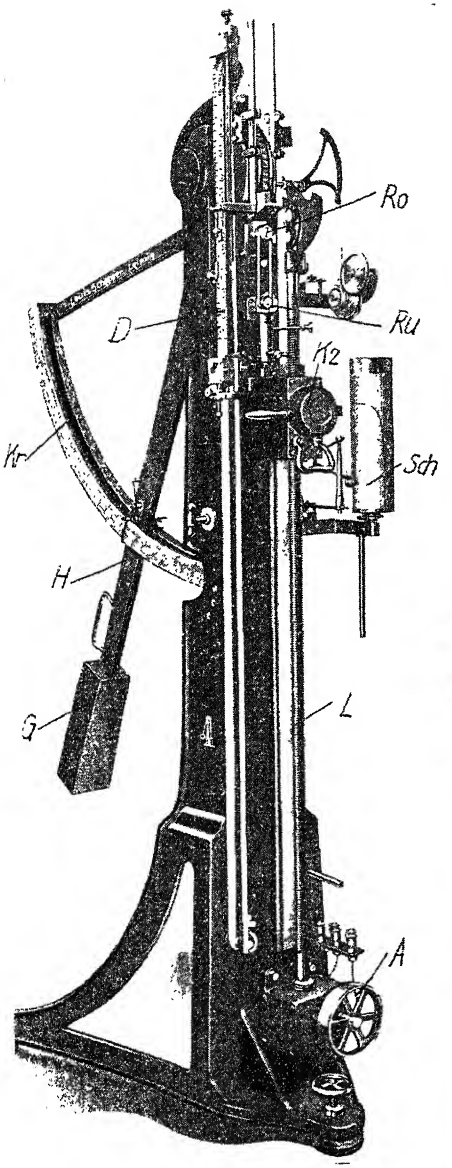


Figure 130 (Above)—Schopper-Dalén testing machine.

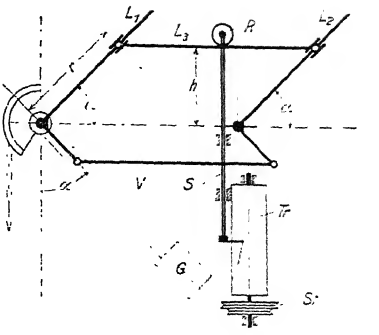


Figure 131—Sketch of the adjustable recording apparatus of A. Schob.

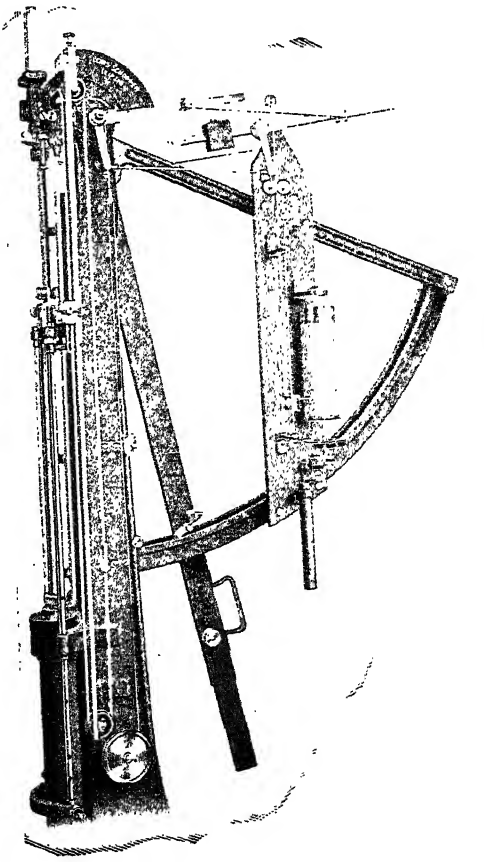


Figure 132 (Right)—View of A. Schob's recording apparatus.

L_2, L_3, V, R, and S are only of structural importance and serve to record the force on the drum in terms of the equation

$$r. \sin \alpha = C \frac{1}{f_o} \sin \alpha$$

in which C is a constant and f_0 is the original cross section. To permit h to remain equal to $r \sin \alpha$, the horizontal bar L_3 must move up and down parallel to itself. To accomplish this, two bars, L_1 and L_2, are necessary. They always turn through the same angle α because the connection bar V is of the same length as the distance between their axes of rotation. Naturally the length of L_3 must also be the same as the distance between the axes of rotation of L_1 and L_2.

Only the vertical motion of L_3, and not the horizontal motion, is to be carried over to the pencil and drum. This is accomplished by having the pencil holder (which is permitted to move vertically only) hanging from L_3 on the easily turned roller R. The constant C in the above formula depends on the unit chosen to represent 1 kg./sq. cm. on the recorder. Since two different units are possible with the Schopper machine, two constants, C_1 and C_2, are necessary, and correspondingly, the bar L_1 has two scales for use with and without the pendulum weight. By setting r at different lengths, the resulting changeable moment $r(L_3 + R + S)$ would cause incorrect readings to be obtained, were it not for the fact that the moment is equalized by the movable weight (*see* Fig. 132) on the prolongation L_2. The divisions of the scale for this counterweight are marked in square centimeters (cross section of the sample) for convenience, just as is that on L_1. The invariable moments of L_1, L_2, and V are equalized by a stationary counterweight.

Since the diameter of the ring which has been stamped out varies within such narrow limits that the theoretical diameter may be used without correction, the adjustment as provided for the recording of stress may be dispensed with on grounds of structural simplicity. Moreover, the adjustments possible in connection with the recording of the elongation may be limited to two steps; namely, that corresponding to the usual standard ring of 44.6 mm. inside diameter, and that corresponding to the small standard ring of 36.6 mm. inside diameter. The elongation (the difference in movement of the upper and lower rollers) is transmitted from the machine to the recorder as a rotation of the drum Tr, use being made of a fine steel wire and the two-step pulley St in the process. With the usual standard rings, the wire runs on the large step; with small standard rings, it is changed to the small step. By means of this change the zero point of the drum is automatically set to correspond to an elongation of about 22 per cent, which is the amount of preliminary elongation given to the small standard rings when placed on the rollers in the starting position.

American Machines

Various details of the testing machine used by the United States Bureau of Standards [30] are shown in Figures 133 to 138.

The circular issued by the Bureau is quoted as follows:

"The dynamometer 1 (Fig. 133) having a capacity of 125 pounds (about 57 kg.) and graduated to one-fourth pound, is attached to the upper end of column 2, which is slotted to receive the rack 3, carrying the eccentric grip 4 at its upper end. The machine is operated by a one-twelfth horse-power motor, which is belted to the stepped pulley 5. A worm on the pulley shaft drives a worm wheel which is geared to a spur (not shown)

[30] *Bur. Standards, Circ.* **No. 38, 5th Ed., p. 48, (1927).**

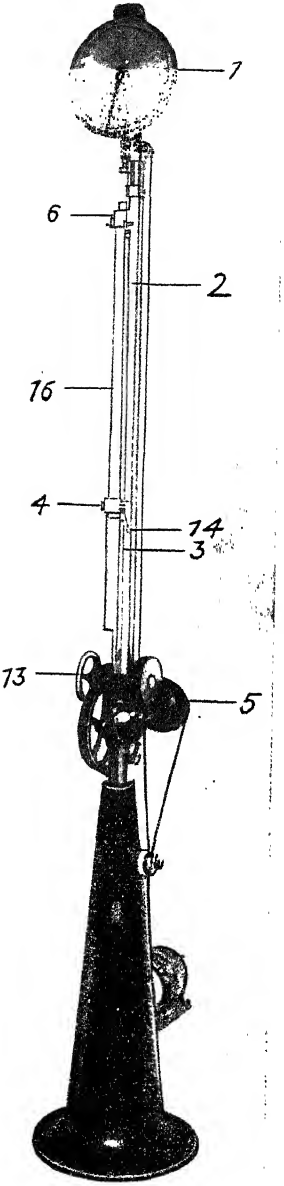


Figure 133—Full view.

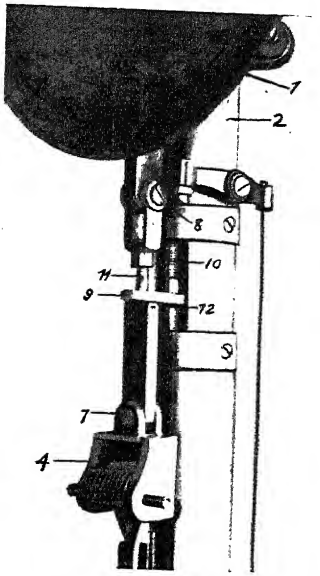


Figure 134—Detail, illustrating method of attaching grip and device for preventing recoil of spring.

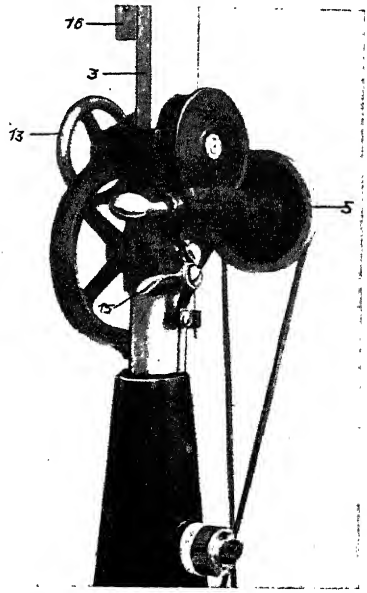


Figure 135—Worm drive and releasing mechanism for rapid return.

Figures 133-135—Machine for testing the tensile strength of soft rubber (Bureau of Standards).

inside of column 2. The eccentric grip 4 (Fig. 134) is attached to the dynamometer through pin connections 7 and 8. The plate 9 serves to prevent recoil of the springs when a specimen is broken, and acts in the following manner: The rod 10, which is rigidly attached to column 2, passes with very little clearance through a hole in the back of plate 9. The front of plate 9 is slotted to receive the rod 11, and is supported by the shoulder 12. As tension is applied to the specimen, plate 9 is free to follow the shoulder 12, and passes down over the rod 10, but when the specimen breaks the upward pressure of the shoulder 12 causes the plate to bind on the rod 10, thus holding the springs under the maximum tension. Hence the pointer of the dynamometer remains at the maximum load when a specimen breaks. The load having been recorded, the upper grip is pulled downward (by means of the hand wheel 13 and hooks 14, if necessary, Fig. 133) to relieve the pressure of the shoulder 12 against plate 9, and at the same time the rear end of the plate is raised to release the rod 10. The tension of the springs may now be relieved by allowing the grip to rise, and the pointer is returned to zero.

"At the end of a test, the worm and gear are disengaged by means of the spring clutch 15 (Fig. 135), and the rack is rapidly raised by hand to its initial position.

"The stepped pulleys provide for different speeds to meet the requirements of experimental work.

"Elongation between gauge marks on the specimen may be measured on the scale 16, attached to column 2, but to do this requires the services of two operators. A simpler and equally accurate method is as follows: A wooden scale graduated to one-tenth inch, is held, as shown in Figure 136, in a slightly inclined position at the back of the test piece with its lower end pressed lightly against the rubber just back of the lower gauge mark. As the rubber is stretched the eye follows the scale just back of the upper gauge mark. With a little practice the elongation at break can be measured with a fair degree of accuracy."

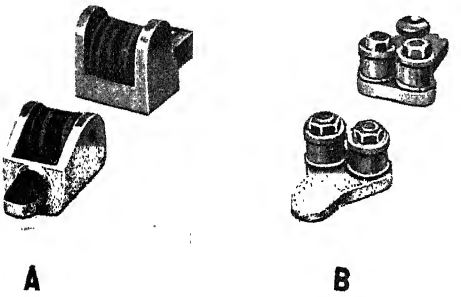
Indubitably these methods of measuring elongation seem more primitive than the automatic method used with the Schopper machine. The deficiencies involved in measuring elongations on bar-shaped samples in this way have been thoroughly discussed on p. 527. The contrivances shown in Fig. 137A are used in the United States Bureau of Standards for gripping the bar-shaped samples. In each of these grips, there are a number of disks set eccentrically on a pin. These eccentric disks tighten automatically as the tension on the rubber sample is increased. In order to hold the rubber sample more firmly, the edges of the disks are ribbed. It is doubtful whether this type of fastening avoids breaks in the ends of the sample or the tendency to slip out of the grips. Investigations in the Materialprüfungsamt with such grips, using bar samples of pure rubber-sulfur mixes 6 mm. in thickness, did not give satisfactory results. The thickness of the sample played a decisive role. In Circular 38 of the Bureau of Standards no information is given concerning the thickness of the sample. The width of ¼" (6.3 mm.) is specified for compounds of high quality. Since the testing machine has a maximum capacity of only 57 kg. (125 pounds), the samples for compounds having an ultimate tensile strength of about 200 kg. per sq. cm. (2844 lbs. per sq. in.) can be only 4 mm. thick.

This testing machine also provides for the incidental testing of ring samples. To obtain as uniform an elongation as possible, a pair of easily turned spools set on ball bearings is used for the upper and lower fastenings respectively, as shown in Figure 138 and Figure 137B.

A more recent American machine is that of Scott. This also has a dynamometer to indicate the stress, and a device to record the stress-strain data automatically with the aid of an electric spark. Since only bar- and strip-shaped samples can be tested, the automatically recorded curve does not give sufficient accuracy.

Testing machines of the type of the Scott Rubber Tester (Henry L. Scott Company, Providence, R. I.) seem to be in much higher favor with American than with German

Figure 136 (Right)—Measurements of elongation by means of a ruler on the tensile testing machine of the Bureau of Standards.



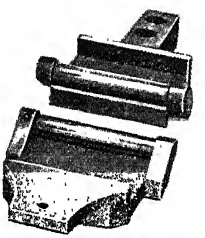
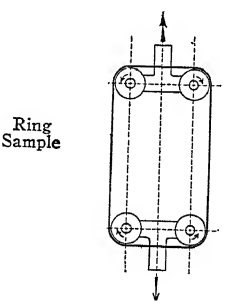


Figure 137—Grips used for bars, rings, and broad strips on the Bureau of Standards machine.



re 138—Tensile tests with ring samples on the Bureau of Standards testing apparatus.

rubber technologists.* The upper portion of the latest model of the Scott machine is shown in Figure 138a. The machine is constructed upon two heavy iron rails and is designed to be fastened to the wall. The dead weight lever principle is used in the construction of the head to give constant accuracy. A 1/6 H. P. motor drives the machine through a gear box which is so arranged that the lower clamp returns instantaneously to the starting position when the machine is reversed after the sample is broken. The pulling member of the lower jaw is of the endless chain type. A compensated head makes it possible to adjust to ranges of gauge from 0.040 to 0.120 inch inclusive.

As the recorder used with this machine is of the electrical type, it is possible for one observer to conduct the tests. A spark controlled by a switch operated by the observer is projected from the pointer through the paper onto the platen. The hole thus burned through the paper registers the load at the particular elongation at the time the circuit was closed. On completion of each test, the platen is moved a small distance by turning the hand screw provided for the purpose, so that the next sample burns a separate line of holes. In this way, one sheet of paper suffices for fifty or more tests.

G. J. Albertoni, working in the laboratories of the Goodyear Tire and Rubber Company, has recently developed a new autographic machine for testing the tensile properties of dumb-bell strips of rubber. (*See* Fig. 138b.) Details in connection with this machine are presented in *Industrial and Engineering Chemistry, Analytical Edition*, **3**, 236-9 (1931). It is so equipped that mechanical correction is provided for variations in the cross-sectional area of test specimens. The personal equation in testing is reduced to a minimum, and the stress-strain curves obtained are directly comparable without any calculations.

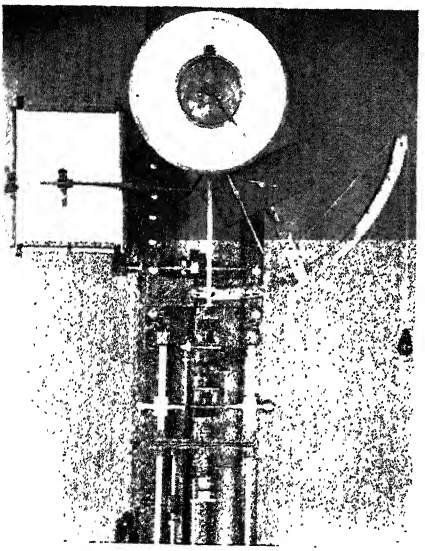


Figure 138a—Latest model of Scott Testing Machine.

Breuil-Cillard Dynamometer

The firm of A. D. Cillard in Paris builds a machine for tensile tests on rubber, textiles, string, rope, linoleum, and celluloid. This machine appears on the market under the name of Dynamometer P. B. (Pierre Breuil). It is very versatile in its uses, since it is provided with arrangements for conducting tension, compression, bending, and other tests. By increasing the load, tests can be carried to the breaking point, or repeated stress tests (protracted tests; *see* p. 584) can be performed. Determinations of the plasticity of plastic materials can also be made on this machine, as well as abrasion

* Translator's note by E. F. S.

tests, determinations of the coefficient of friction, etc. The description here will only consider its use for tension tests on soft rubber.

Figure 139 illustrates the construction of the apparatus. For ordinary tests it is driven by hand, by means of a gear transmission and screw spindle. For protracted tests with repeated stresses, a motor is used with the worm drive *rs*, which is placed under the table. The two shaft supports, *g* and *o*, can be either fastened to the base upon which the machine rests, or be made movable on the guides in the machine bed. The latter arrangement is adopted when repeated stressing of the sample is undertaken. By means of the worm drive *rs* and rod *q*, which has one end attached to the eccentric disk *d* and the other to the shaft support *o*, a to-and-fro motion of the shaft supports *g* and *o* along the base is obtained. This results in an alternate stretching and releasing of the rubber sample held in the grips *e* and *f*. The difference between the greatest and least stretching of the sample can be varied by changing the degree of eccentricity of the disk *d*.

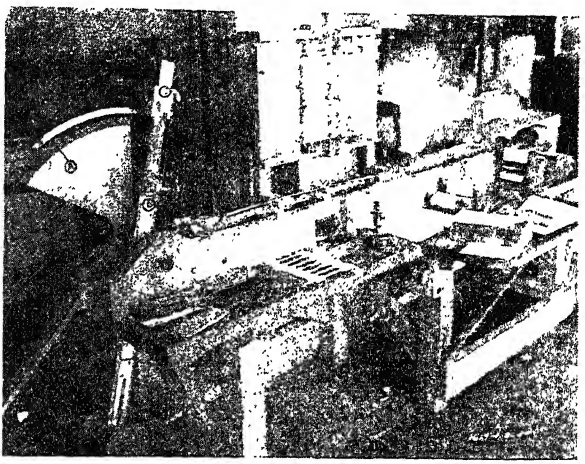


Figure 138b—The tensile-testing machine developed by G. J. Albertoni.

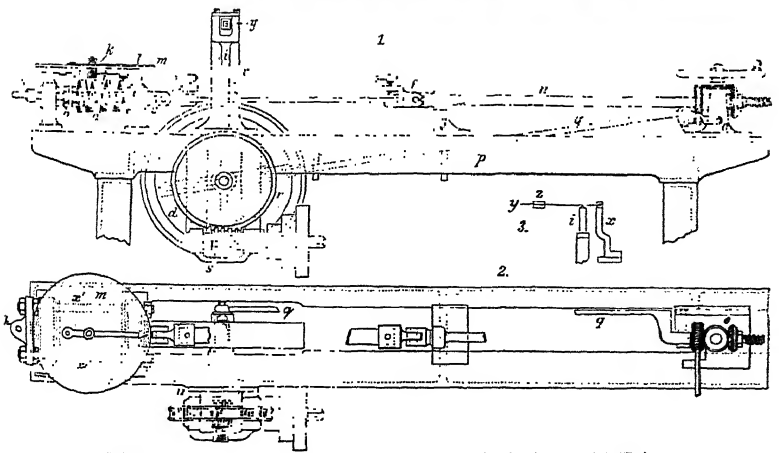


Figure 139—Dynamometer of Breuil-Cillard (P.B.)

The grip *e* is fastened directly to the dynamometer, which consists of a spring balance having a helical spring *a*. The changes in length of the spring are read from the circular scale *m*. When the sample breaks, the spring recovers, but the pointer remains at the farthest point reached. The entire dynamometer of the machine is so built that with the help of the transverse rods *xx'* it is suspended between two small supports *v* and forms a unit which may be taken out of the machine as such. It can easily be hung on a hook, and weights may be applied to it directly when calibrating the scale.

Older Machines

Neither of the machines described immediately below is to be considered important other than from the historical point of view.

An older French machine is that of Delaloe (shown in Fig. 140). The rubber sample in the form of a strip or bar is held in the grips. The motive power is supplied by the hand wheel which operates a screw spindle to which one of the grips is fastened. The other grip is fastened to the dynamometer in a manner similar to that of the Dynamometer P. B. The frame of the machine consists of two parallel guide rods mounted on a base. The holder of one grip moves along these rods.

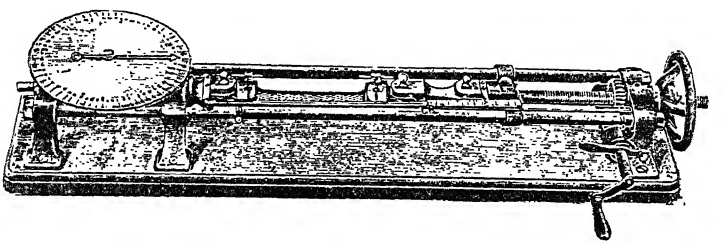


Figure 140—Delaloe's machine.

A similar machine, apparently of English origin, is described by C. O. Weber on page 216 of his well-known book "The Chemistry of India Rubber." This machine, like that of Delaloe, has a screw spindle driven by a hand wheel. Figure 141 shows how the clamps are constructed. They move in the cast iron frame of the machine. A pendulum balance measures the stress on scale *E*. The ratchet device *DH* makes it possible to hold the pointer at the highest load reached. The elongation of the sample is measured by the graduations *K* on the side of the machine frame. In view of the above discussion of bar-shaped samples, this method of determining stress-strain characteristics of soft rubber must be considered inadequate.

No doubt, other machines for testing the tensile properties of soft rubber have been built. So far as is known, they have not made any important contribution to the technique of testing. New designs always repeat the old mistakes in part.

A. Schob's Tester for Rubber Coverings

A. Schob has designed a small instrument to be used especially for testing rubber-covered cable from which the copper wire has been removed. A modification, equipped with an electric motor, is marketed by L. Schopper (*See* Fig. 142). In the original form of this equipment (hand-powered) the sample was

held between two pins, each of which had a diameter of about
of the sample was put through a hole in the pin and then
latter a few times (*see* p. 541). One pin was fastened to
(spring balance) and the other to the spindle which was operated by the motive power of the machine. This manner of holding the sample gave no

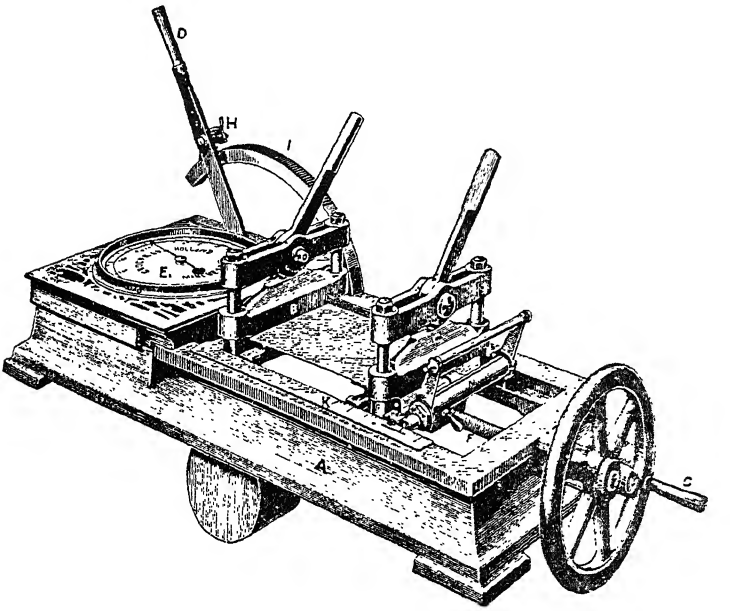


Figure 141—C. O. Weber's Machine.

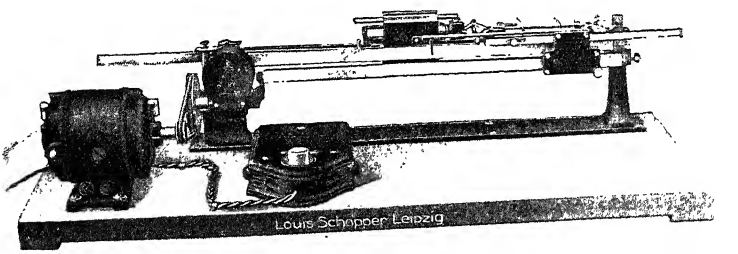


Figure 142—A. Schob's tester for coverings removed from insulated cables.

difficulty due to breaking at the grip, inasmuch as the rubber compound contained only 33 1/3 per cent rubber. (The new Schopper model provides clamps which automatically grip the sample tighter as the tension increases, by means of a scissors-like arrangement.) The innovation on Schob's testing apparatus is in the method of measuring the elongation. Naturally, a reasonably accurate measure of the elongation on this sample can be made only by

following marks on the free part of the sample. The device shown in Figure 143, which allows a pointer to be placed in the middle of each mark, can be operated with one hand. The marks are set at 10 mm. on the original sample, so that both marks remain in the field of vision.

The rack C can be moved in the piece A by turning the knob E which operates the pinion B. This moves the pointer so as to keep up with the movent of the marks. The pointer Z_1 is fastened to the piece A, and Z_2 is on rack C. At the zero point, Z_1 and Z_2 are 10 mm. apart. The millimeter

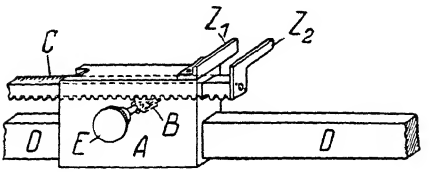


Figure 143—Device for measuring elongation on Schob's tester.

graduation on the rack gives the percentage elongation without any calculation when the original length is 10 mm. Since the marks move in opposite directions, it must be possible to move both of the pointers in the direction of the tension, independently of their distance from each other. To do this, piece A and everything attached thereto may be moved along the rod D. The knob E serves to move A. With very little practice, an operator can use one hand to supply the motive power, and the other to attend to the measurement of the elongation. Since the turning of knob E is stopped at the instant of break, the greatest elongation remains fixed on the scale. During the test, it is not necessary to make readings on the scale, but merely to keep the pointers at the middle of the marks. If points on the elongation curve are desired, two observers are necessary. Although this apparatus was designed especially for rubber insulation, it can be used on other similarly applied material. For that reason it has been described among the general types of testing equipment.

Devices for Tests at High and Low Temperatures

Up to the present time, tensile tests on soft rubber at temperatures above or below room temperature have been performed only occasionally. The necessary enclosures for temperature control have been subsequently built on the machines, since the original construction provided only for conducting tests at room temperatures. (Also *see* page 519.)

The T-50 Test for State of Cure*

A test which can scarcely be considered as a tension test in the usual sense of the word is the T-50 test for state of cure developed by W. A. Gibbons, R. H. Gerke, and H. C. Tingey [*Ind. Eng. Chem., Anal. Ed.*, **5**, 279 (1933)]. The test depends on the observation that for a specific rubber compound the greater the state of cure the lower is the temperature at which chilled, stretched rubber will spontaneously retract. The rubber is "racked" at a low temperature and is then gradually heated. The T-50 value is the temperature at which the rubber has retracted to such an extent that it has lost 50 per cent of its original elongation. The T-50 value for raw rubber is approximately $+18°$ C. The reader is referred to the original article for details regarding the procedure of the test.

* Translator's note by V. N. M.

The T-50 test is said to simplify the estimation of state of cure. It is not suitable for use with types of rubber which cannot be stretched. It has been used for testing the activity of accelerators, and for studying the effect of such variables as temperature of presses and mold lag on the state of vulcanization. The test has an advantage over the usual tensile tests in that the width and thickness of the test piece need not be measured, but on the other hand it does not permit the selection of optimum cures or the cure in a series of cures which will best resist abrasion or deterioration. Although the test gives good correlation with the results of determinations of combined sulfur in many cases, there are sometimes large deviations from this correlation.

Compression Tests

The True Compression Test (Investigations by Stévart)

Specific standard methods of conducting compression tests with soft rubber have not been developed, since an evaluation on the basis of such tests is seldom necessary. In case tests are required to determine elasticity and deformation under compression, they can in general be conducted on the finished article (rubber buffers and packing rings, for example). Any press will be suitable if the compressive force, which for the most part will be small, can be measured with sufficient accuracy. In general, the measurement must be confined to the determination of the total deformation of the sample under a given load or the residual deformation after stress, since with soft rubber it is not possible to determine under compression a breaking load which may be used as a measure of quality.

Several articles on this subject are to be found in the older technical literature.

P. Breuil [31] gives a survey of a number of investigations by Boileau, M. Hovine, M. Debonnefoy, Werder, and Stévart, relating to compression tests on rubber. Of these, the work of Stévart is of the greatest general interest. Therefore, his work, insofar as it had to do with the shape of the sample and method of test, is discussed here at length. That part of Stévart's researches which was concerned with the general physical properties of rubber under compression and the attempt to develop a mathematical formulation of the existing relations, has already been treated by Hock in the section on the "Physics of Rubber" (p. 400).

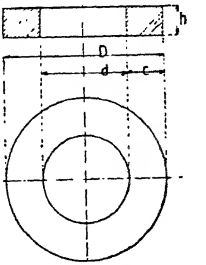


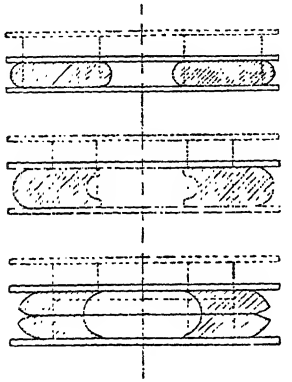
Figure 144—
Stévart's sample for
compression tests.

investigations, Stévart [32] used rubber rings of the form shown in Figure 144, and carried out the tests in a simple screw press. His method was to lay several rings of the same dimensions on each other, with thin steel plates intervening to keep them from being in actual contact. These plates had such large diameters that, even when the rubber rings were under great compression, the increase in cross section of the latter was insufficient to allow their outer circumferences to extend over the edges of the plates.

[31] *Caoutchouc & gutta-percha*, **2**, 6-9, (1905).

[32] *Bull. musée ind. Bely.*, **59**, 5-15 (1871); **63**, 5-15 (1873).

Stévart established that the change in the outer form of the rubber ring is dependent on the dimensions, particularly on the ratio of the height of the ring *(h)* to its width *(c)*. (*See* Fig. 144.) If the ratio h/c is smaller than 2/3, the change in form is similar to that shown in Figure 145. With a ratio greater than 2/3, the compressed ring has the appearance illustrated in Figure 146. If two rings are placed on each other (without intervening steel plates) and compressed, their form becomes that of Figure 147.



Figures 145-147—
Changes of form of rubber under compression (according to Stévart).

In determining the effect of the dimensions of the sample on the compression of rubber rings, Stévart worked with rings of various sizes, made of a rubber compound having a specific gravity varying between 1.059 and 1.070. The compression of all samples was ascertained at loads of 2,000, 2,500, 4,000, 5,600, and 7,000 kg. In view of the thoroughness characterizing all of Stévart's work, it may be assumed that he recognized the influence of time, and consequently determined the compression of all samples after that had been under load for the same interval of time. A statement to that effect does not appear in the work.

Table 7 shows the dimensions of samples which were used. From this table, it is apparent that Stévart made use of the four series of dimensions listed below.

1. Numbers 1-8; the same dimensions, except for variations in the original height *h*.
2. Numbers 9-13; varying widths *c* (*see* Fig. 144), and inner diameter *d;* constant diameter *D* and height *h*.
3. Numbers 14-19; constant width and height, but varying outer diameter *D* and inner diameter *d*.
4. Numbers 20-22; constant height *h*, but varying widths *c*, with corresponding variations in inner and outer diameters.

Stévart expressed the results of the investigation in terms of a mathematical relation which is more fully discussed in the section on "Physics of Rubber" (Hock, p. 400).

These experiments by Stévart show that even in compression tests, the dimensions of the sample exert a great influence on the results of the test. Of course, the tests are based only on one shape of sample (the ring).[33]

[33] The investigations of A. Martens ("Handbuch der Materialienkunde für den Maschinenbau," Section 17, p. 166, J. Springer, Berlin, 1898) furnished considerable information regarding the influence of the shape of the sample on the results, in the case of cylindrical and cubical shapes, such as those used in testing metals, wood, etc. Martens studied the influence of the shape of the sample on the shortening (—ε) due to compression, with cylinders and prisms of ingot iron having different cross sections (*f*) and heights (*e*) and

TABLE 7.—*Dimensions of the Samples Used by Stévart in His Compression Tests.* (All measurements are given in mm.)

Series (*See* Fig. 144)	Test number	Outer diameter D	Inner diameter d	Average diameter d'	Width $C = \frac{D-d}{2}$	Area $S = \pi . d' . C$	Height h*	Remarks
I	1	100	40	70	30	6597	6.0	4 identical rings†
	2	100	40	70	30	6597	10.7	3 rings as with 1
	3	100	40	70	30	6597	15.4	2 rings as with 1
	4	100	40	70	30	6597	20.3	
h varies,	5	100	40	70	30	6597	25.0	
c, d, D	6	100	40	70	30	6597	30.4	
constant	6a	100	40	70	30	6597	30.3	
	7	100	40	70	30	6597	36.0	
	8	100	40	70	30	6597	30.8	
II	9	129	89	109	20	6849	29.8	
	9a	130	89	110	20	6912	30.4	
c, d vary	10	130	80	105	25	8247	30.5	
D, h con-	10a	130	81	105.5	24.5	8120	30.2	
stant, with	11	130	70	100	30	9425	30.0	
the excep-	11a	130	70	100	30	9425	29.8	
tion of h	11b	130	70	100	30	9425	30.0	No. 18, Series III
in 12 and	12	130	50	90	40	11310	50.0	
12a	12a	130	50	90	40	11310	49.2	
	13	130	30	80	50	12566	30.5	
III	14	60	0	30	30	2827	30.2	
	15	80	21	50.5	29.5	4680	30.5	
	16	100	40	70	30	6597	30.3	
	16a	100	40	70	30	6597	30.4	No. 6, Series I
D, d vary	17	118	60	89	29	8102	30.1	
C, h con-	18	130	70	100	30	9425	30.0	
stant	18a	130	70	100	30	9425	29.8	No. 11a, Series II
	18b	130	70	100	30	9425	30.0	No. 11 , Series II
	19	139	78	108.5	30.5	10328	30.5	
IV	20	80	40	60	20	3768	30.4	
c, d, D vary	21	92.5	29.5	61	31.5	5933	30.2	
h constant	22	100	21	60.5	39.5	7504	30.2	

* This h and also the one in Fig. 144 correspond to the H in the formula on p. 400; i. e., the height of the unstressed sample.
† With separating plates.

Stévart gives several more directions of importance in connection with the practical performance of the compression test. If several rubber disks are laid on each other but are kept separated by sheets of metal, it is very important that the surfaces of the metal sheets be polished, so that the friction at the end surfaces of the samples will not be increased because of roughness or uneven spots. In addition, the diameter of the metal disks must be sufficiently large so that the rubber samples, which are greatly enlarged in cross section by pressure, will not protrude over the edges of the metal, even under the greatest compression load to be used in the test. The fact that the increase in the cross section of the sample is accompanied by a decrease in the inside diameter (*see* Fig. 145), must be kept in mind in making plans for the test

also the following ratios:

$$\frac{1}{n} = \frac{\sqrt{f}}{l} = 2.00 : 1.33 : 1.00 : 0.80 : 0.40 : 0.20.$$

The compression ($-\epsilon$) was found to be influenced but little by the dimensions of the sample, provided the dimensions were not such as to cause the value of the ratio $\frac{1}{n}$ to differ too much from unity. With identical loads per unit cross section, and the same ratio $\frac{1}{n}$ the shortening for the circular cross section was less than that for the square cross section.

equipment, if any hindrance to extension toward the inside is to be avoided. According to Stévart, this requirement is met by making the inside diameter d of the sample greater than the height h. Of course, care must be taken to center the samples properly and to keep them centered during the experiment. Stévart used separating disks of the shape shown in Figure 148 for this purpose. The grooves in the disks hold the sample centered with respect to the means of applying the load.[34]

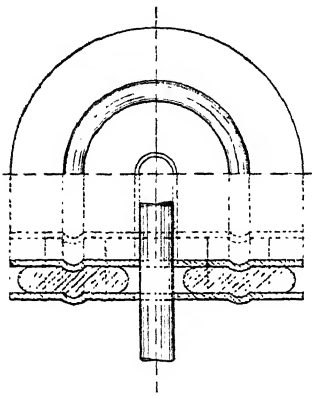


Figure 148—The special method of holding the sample used in Stévart's compression tests.

Penetration Tests

In testing metals, the Brinell method of pressing a sphere into the surface as a means of determining the resistance to penetration has been quite commonly adopted. Brinell hardness, in conjunction with tensile strength and elongation, has become of the greatest importance as a means of evaluating metals. It was expeditious, therefore, to apply this proven method to the problem of testing rubber. For this purpose A. Martens designed a small instrument with which the resistance to penetration of rubber slabs, particularly of soft vulcanized rubber, may be determined, using the Brinell method of pressing a ball into the sample. This instrument is illustrated in Figure 149. The circular piece remaining after stamping out the normal ring for tension tests (*see* p. 530) can generally be used to advantage as the sample. The diameter of the sample is thus 44.6 mm. and the thickness normally 6 mm. However, the instrument may be used on other samples if they provide a sufficiently large, level, horizontal space so that the base of the instrument will be steady when placed on the sample. A steel ball with a diameter of 5 mm. is attached to the end of the short horizontal arm of a bell crank, the fulcrum of which is on the lower part of the base of the instrument. The long vertical arm constitutes the indicator, and shows ten times the vertical motion of the ball (or in other words, the penetration) along a scale fastened to the upper part of the stand. A vertical rod rests on the steel ball. Various weights can be placed on the upper end of this rod.

With the largest weight which Martens suggested for use with the instrument (100 grams), very soft rubber-sulfur mixes having no other compounding ingredients give a penetration of about 0.45 mm. on a slab 6 mm. thick.

[34] See "Physics of Rubber," p. 400, for several later investigations of compression.

Harder compounds (solid tire stock, for example) give a penetration of about 0.15 mm. The impression caused by the ball remains only as long as the weighted ball acts on the soft rubber sample. This is true except for a small fraction similar to the elongation set δ' in tensile hysteresis (p. 564) and in elasticity tests (p. 561). The measurement of penetration must therefore be made while the pressure is being exerted. The test on rubber differs in that respect from the Brinell test on metals. The depth of penetration

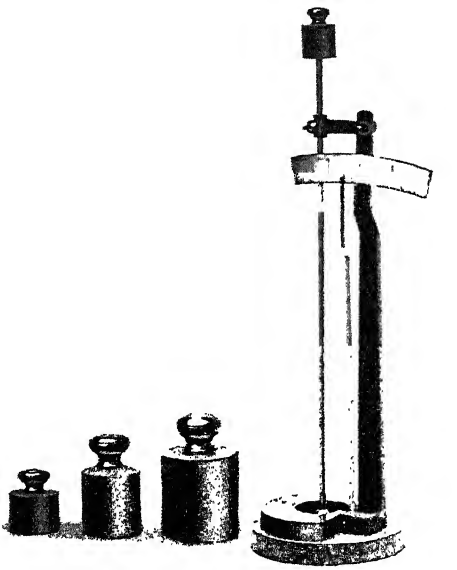


Figure 149 — The apparatus of A. Martens for the determination of the hardness of soft rubber by pressure of a sphere (as in the Brinell test).

increases as long as the pressure is effective, although this "after-effect" is different for different compounds, and particularly for varying degrees of vulcanization. Therefore, the reading of the penetration is always made after identical intervals of time following the application of the weighted ball. In the Materialprüfungsamt, 5 and 30 seconds are used. The "after-effect" (i.e., the difference between the penetrations after 5 and after 30 seconds) is greater when the degree of vulcanization is less.

The volume of material displaced as the ball penetrates the sample is naturally greater with softer samples. Therefore, the ball must not be placed too close to the edge of the sample, particularly if the latter is relatively soft. The thickness of the material under the ball influences the results greatly, the effect being greater with soft than with hard compounds. In the application of the ball penetration test to the factory control of the manufacture of rubber rolls, wide differences in thickness are encountered. Figure 150 shows empirically determined relationships between depth of penetration and thickness of the sample.[35]

This small instrument of Martens', which has just been described, is very simple in performance, but is satisfactory only in the hands of an experienced

[35] These tests were conducted in the laboratory of the Vereinigten Berlin-Frankfurter Gummiwaren-Fabriken. The authors owe these hitherto unpublished results to the kindness of the director, Mr. Gottschalk.

operator. For more general use, a design like that of Schopper's is recommended. In this apparatus (Fig. 151), a stand is built on a substantial base

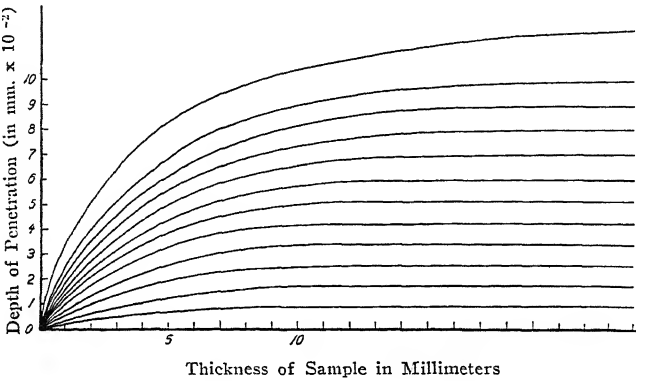


Figure 150—Dependence of the depth of penetration on the thickness of the sample, when using different loads on the ball of the hardness tester. (According to Gottschalk.)

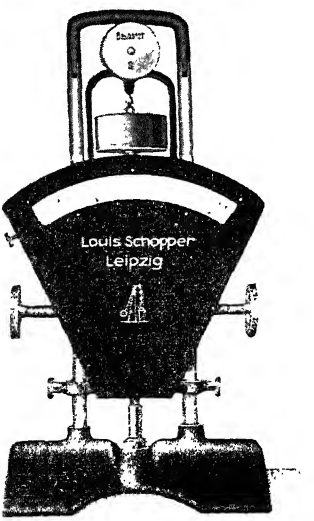


Figure 151—
Hardness tester built by Schopper.

plate, and the sample is placed on the plate. (To use the instrument on large pieces, suitable attachments are provided without a base plate.) Naturally, care should be taken that the samples lie perfectly flat on the base, as otherwise the readings of the depth of penetration will be in error. As is evident from the arrangement shown in Figure 151, the movement of the ball is measured with respect to the location of the upper surface of the sample before pressure is applied, and not (as in the Martens' test) with respect to an upper surface which changes as the test progresses. Bending of the sample would, of course, give misleading results. A load of 1000 grams is used on

the Schopper machine, because the friction in the instrument produces too high a percentage error with a load of 100 grams. The diameter of the ball is made 10 mm. instead of 5 mm., so that the specific pressure under the ball does not become too great with the 1000 gram load.

The instrument of Breuil's (built by A. D. Cillard, Paris) for the determination of "rebound" elasticity of soft rubber, can also be used to determine penetration by suitable changes in several parts (*see* p. 549). Because of this added use, this instrument is also called an Elasto-Durometer. Figure 152 shows a view of the apparatus when it is used to determine depth of penetration. A cross section is illustrated in Figure 153. In the brass tube *D*

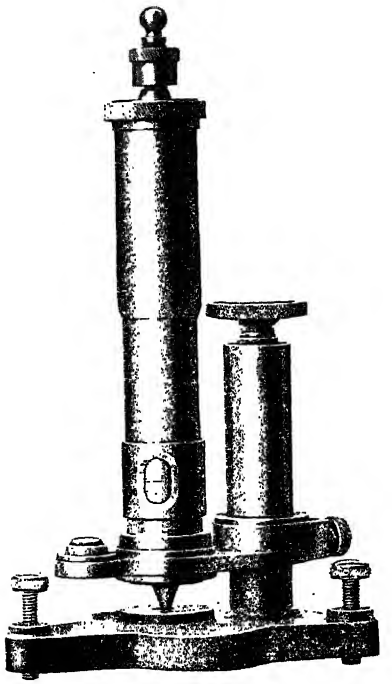


Figure 152—Durometer "P. B.," made by A. D. Cillard of Paris.

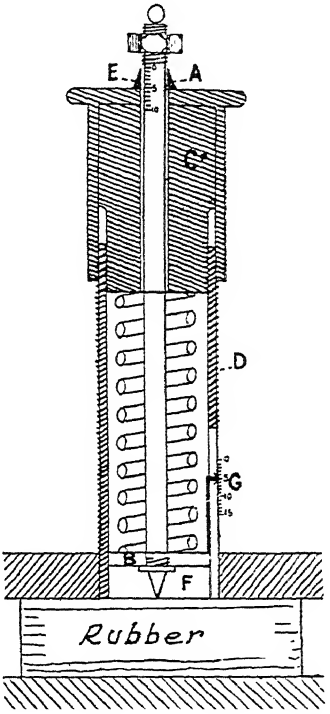


Figure 153—Cross section of Durometer "P. B." of A. D. Cillard.

is a helical spring. Its upper end is held by the plug *C* which screws into the tube *D*. The lower end rests against a plate *B* which moves freely in the tube. The compression of the spring, or the pressure which the conical tip *F* of the rod *A* exerts against the sample lying under it, is measured at *E* by means of the graduations on the rod *A*. Graduations on the tube *D* make it possible to measure at *G* the depth to which the tip presses into the sample in tenths of a millimeter. The measure of hardness is derived from the ratio P/E, in which E is the penetration and P the restoring force of the spring. Several results of hardness determinations with various rubber compounds are reproduced in Table 8.

TABLE 8.—*Penetration Tests with the Durometer P. B.*[5]

Constitution of the compound			Time and temperature of vulcanization	Thickness of the sample (in mm.)	Penetration E of tip (in mm.)	Force P pressing tip into the sample (in kg.)	$\frac{P}{E}$
Per cent Rubber	Per cent Sulfur	Per cent Other Materials					
97	3	....	3 hrs. 15 min. at 130° C.	5.0	4	2.400	0.60
96	4	....		5.0	4	1.800	0.45
97	3	....		5.0	4	1.560	0.39
96	4	....		5.0	4	1.680	0.42
62	6	....	1 hr. 20 min. at 135° C.	5.5	4	1.920	0.48
87	13	32	2 hrs. 45 min. at 135° C.	6.0	4	2.700	0.67
76	11	13		4.8	4	4.200	1.05
48	16	36	2 hrs. at 135° C.	5.0	4	3.000	0.75
48	6	46	1 hr. 30 min. at 126° C.	5.0	4	6.600	1.65
48	6	46		5.0	4	7.800	1.95
50	3	47	1 hr. 30 min. at 135° C.	5.0	4	6.000	1.50
27	2	71	1 hr. 30 min. at 130° C.	4.5	3	14.400	4.80
10	2	43	1 hr. 30 min. at 126° C.	4.5	0.8	14.400	19.00
		45					

[5] *Caoutchouc & gutta-percha*, **5**, 2190 (1908).

used for the determination of
The principle is
lie merely in the

details of construction.[36]

HOLLOW SPHERE TEST †

The relation existing between a compressive force and the two-dimensional stretching forces necessary to effect the same deformation in rubber as the compressive force itself has formed the basis of a method for measuring compression stress-strain used by J. R. Sheppard and W. J. Clapson [*Ind. Eng. Chem.*, **24**, 782 (1932)]. A hollow, thin-walled sphere of rubber (balloon) is inflated, and the gas pressure and dimensional measurements are followed during the inflation. From these data is calculated the compressive force which would be required to give the same degree of shortening in one direction as is actually produced by transverse stretching forces. The method has the advantage of being free from the errors due to friction or to nonuniform deformation, but the disadvantage of very limited application in the present stage of its development. In fact, the investigators did not claim that they had perfected the technic of the test at the time their paper was published.

An interesting inference from the work carried out by Sheppard and Clapson is that the compression stress-strain curve of rubber is continuous with the ordinary elongation stress-strain curve, and that the complete stress-strain relationship should be expressed as a continuous curve having an elongation branch and a compression branch. Nothing other than an entirely empirical relationship between the two branches of the curve seems to exist and it has not been found possible to calculate compression stress-strain from one-dimensional elongation stress-strain data.

[36] See E. R. Dawson, "The Hardness Testing of Vulcanized Rubber" [*Trans. Inst. Rub. Ind.*, **3**, 217 (1927)]; also E. C. Zimmerman and [illegible] der [*Ind. Eng.* [illegible]

† Translator's note by

Experimental Methods for Determining the Elastic Behavior of Soft Rubber

General Notes on Elasticity [37]

In the case of a substance which is used mainly because of its unusual elastic properties, a quantitative determination of the elasticity is naturally important. Elasticity is that property of a body which causes it to recover its original shape after the external force which produced the deformation has been removed.[38] If this capacity for recovery were never present or always present 100 per cent, a method for measuring it would not be required. In reality, it is never missing nor is it ever present 100 per cent, and therefore its size must be measured. What measuring stick is to be used for this? Should the deformation set ("Elongation Set" [39] δ', Fig. 157, p. 564) of tension tests, which remains after a complete release of the sample from load, be used, or should the loss of external mechanical energy (force × distance), which is measured between the loading and unloading of the test sample (comparable to hysteresis loss in the same figure), be the basis of elasticity measurement?

The proper measure is deformation set in the case of static stressing, and hysteresis in the case of dynamic stressing. There are methods of testing for both. However, it should be kept in mind that these two methods are not comparable, even though their results usually are parallel, for the first deals with linear measurement, and the second with the measurement of mechanical work. With the breaking tests, the limit to which the stressing can be carried is given by the actual break. It is necessary to set a limit with all other tests, which, by their very nature, must avoid a complete break, at least with the first stressing. The stress-strain diagram of soft rubber (*see* p. 517) does not resemble that of wrought iron, which has characteristic points corresponding to the elastic limit and to the yield point.[40] The magnitude of the stresses in use is also not very accurately known. One is therefore advised to set an arbitrary limit of the stressing, in such tests as elasticity tests on soft rubber. This limit should not be chosen too low as too favorable a result may be obtained, and it should not be chosen too high, since a premature break in the sample may be encountered.

Determination of Elasticity by Measurement of Deformation Set

Stretching Tests

In accordance with the preference for stretching tests for determining the strength and deformation of soft rubber, tension stressing is preponderantly used for the kinds of elasticity determinations which depend on the measurement of deformation set. Since the breaking point is seldom approached in this test, the question of whether ring or strip (p. 540) test samples are to

[37] See also p. 394 and the following pages.

[38] Accordingly, in the following discussion, if another meaning is not explicitly expressed, this definition refers only to the so-called solid bodies, and not to liquids or gases. Compare also with A. Schob's article "On Elasticity," *Gummi-Ztg.*, **40**, 624 (1925).

[39] With soft rubber the expression "permanent elongation" ("permanent set"), used in the testing of materials, is to be avoided, because *the elongation is not permanent, but decreases* more or less in relation to time, according to the compounding and the degree of vulcanization (elastic after-effect).

[40] See Martens, A., "Handbuch der Materialienkunde für den Maschinenbau," Vol. I, 21, J. Springer, Berlin, **1898.**

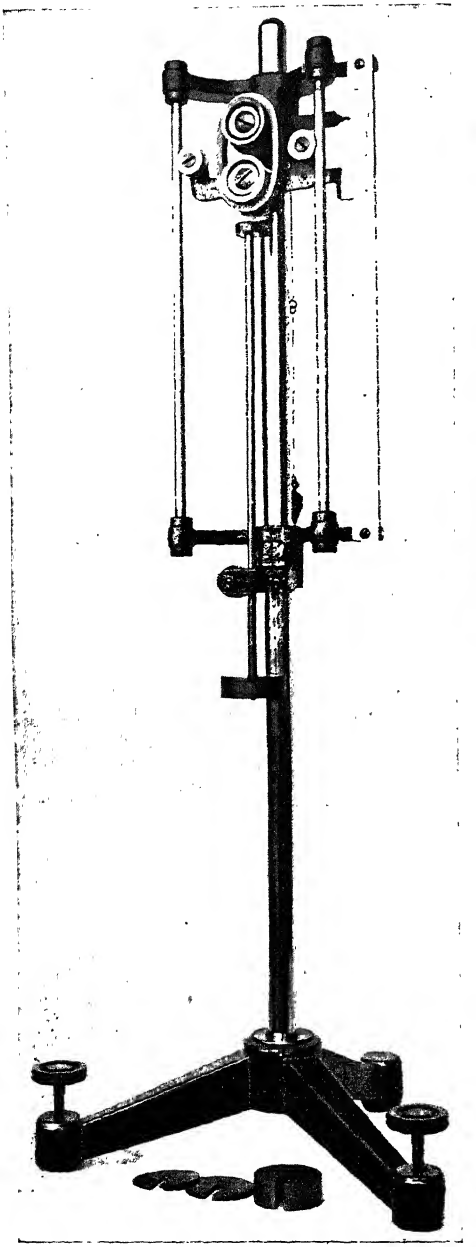


Figure 154—The Martens-Schopper machine for measuring elongation.

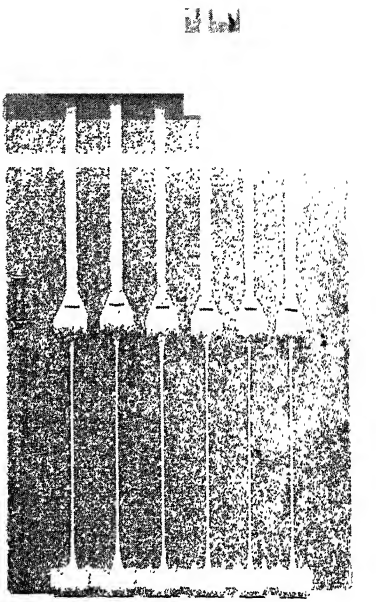


Figure 155—The stretching apparatus of the Bureau of Standards.

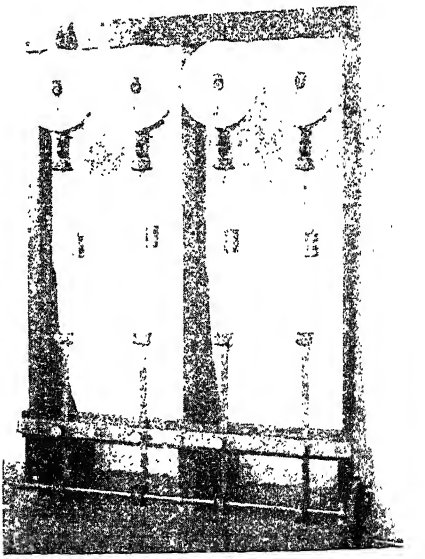


Figure 156—The Bureau of Standards apparatus for the measuring of change in tension at constant elongation.

be used, is of little importance. The authors prefer ring samples except in special cases. As was mentioned before, the choice of the degree of stressing is optional. In the Materialprüfungsamt as a rule, the tension tests are carried out at 50 per cent of the average breaking elongation of the soft rubber concerned. The sample is stretched this amount for one hour, then released, and the elongation set δ' is measured. Since the amount of the set depends on the time elapsed since the release, the set is measured after two time intervals following the release; namely, after 5 minutes and after 24 hours. The Schopper-Dalén machine can be used for single tests. A testing machine built in a fashion similar to the apparatus illustrated in Figure 154 is still better for the determination of elongation set.

The set is determined as follows: The ring is placed over the two easily turning rolls, which are of the same diameter as the ones in the Schopper-Dalén machine. The knurled upper roll, the axle of which rests on the frame, is so loaded while being turned that the tension rolls reach their zero positions (with normal rings of 44.6 mm. inside diameter, and 70 mm. inner circumference, this zero setting corresponds to a distance of 30 mm. between roll centers).[41] This loading, which depends on the degree of stiffness of the sample, is recorded, and is again replaced before the sample is put on, after the measurement of the 5-minute and 24-hour elongation sets. Since, especially with very soft and under-cured compounds, the influence of time is disturbing, even with the small weights which can be considered for this machine, the reading of the scale should be done as quickly as possible. The reading should be made within a few seconds after the loosening of the lock screw and the gentle lowering of the lower roll, while the upper roll is turned by hand (best of all with the left thumb). Naturally, it is not possible to select the small loading weights for the test in a few seconds.

If too small a weight has been chosen, the load is immediately released, additional weight is added, and then by turning the upper roll, the lower roll with its carriage is gently lowered. The use of too large a weight and the over-stretching of the sample in the process of placing it in the tension apparatus, are to be avoided. It is best to reject the sample in such a case.

A practical apparatus for the simultaneous stretching of a number of strip samples is described in Circular 38 of the Bureau of Standards. This apparatus is illustrated in Figure 155.[42] A crank, which needs no further explanation as is seen from the figure, is used to obtain the simultaneous stretching of the six samples. The Bureau of Standards usually uses a duration of stretch of 1 or 10 minutes. By measuring with a ruler the distance between the marks made previous to the test, the set of the strip samples may be determined.

The determinations which have been discussed up to this point are correctly designated as stretching or tension tests, because they use as a measure of stress a definite elongation which is kept constant during the testing. A method which is much less frequently used is that of loading with a definite weight, the resulting change in length being measured. Tests are carried out in this manner in the Materialprüfungsamt, using very small loads (2 per cent of the breaking load) but very much longer loading periods. In such

[41] It is more expedient to set the marker on the holder of the lower roll at 70 mm. than at 30 mm. when the distance between the centers of the rolls is 30 mm. In this way the scale gives a measure of one-half the inner circumference of the ring directly, even with rings which are not normal rings.

[42] See *Bur. Standards Circ.*, No. 38, Fig. 20, p. 53 (1927).

a test the aging of the sample finally plays an important part (*compare* with Figs. 176 and 177, p. 588).[43]

With constant elongation, the original tension drops off gradually. This lowering of tension offers also a measure for the dependence of the elastic behavior on the time, which is generally designated as "elastic after-effect." In Figure 156 [44] is shown an apparatus which is used by the Bureau of Standards to obtain the lowering of tension as a function of time, with constant elongation of a strip sample. The upper clamp is fastened on a spring dynamometer. The crank, in contrast to the one in Figure 155, is placed at the bottom. A counterweight, which is visible at the right center behind the sample, is required to relieve the sample of the weight of the lower carriage.

Compression Tests

The determination of the elastic behavior by measuring the deformation set after long duration of compression, analogous to the tension test, is seldom used in pure material research, but is specified now and then in tests for packing rings and similar soft rubber rings.

Determination of the Elasticity by Measurement of the Work of Deformation

The Hysteresis Test

If in a tension test the sample is not stressed to the breaking point, but is unloaded again, the relation between elongation and tension during the unloading is illustrated by the broken line in Figure 157. The area A_r (horizontally and vertically hatched) under the unloading curve, represents the recovered mechanical work, or the external work given off by the sample during the unloading. Area A_r is smaller than the total area A_a by a difference equal to area A_H. Area A_a is the total area (designated by horizontal lines) under the loading curve, and represents the work input during the stressing of the sample. A_a minus A_r gives the loss of work between loading and unloading; i. e., the hysteresis loss.

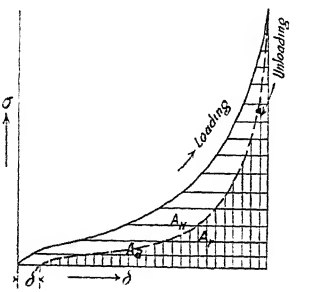


Figure 157—Hysteresis.

The following equation

$$\frac{A_a - A_r}{A_a} = \frac{A_H}{A_a}$$

gives the hysteresis loss in relation to the energy expended.

The ratio $\frac{A_r}{A_a} = \frac{\text{Recovered work}}{\text{Expended work}}$

(usually multiplied by 100 to give an expression in per cent) is called "elastic efficiency" by A. Schob,[45] (and designated η_{el}), since the ratio of two quan-

[43] See Martens, A., *Sitzber. preuss. Akad. Wiss.*, 14 (1911).

[44] *Bur. Standards Circ.*, No. 38, Fig. 21, p. 54 (1927).

[45] *Mitt. Materialprüfungsamt, Berlin-Dahle* 228 (1919); also *Gummi-Ztg.*,

tities of work is generally designated as efficiency. The theoretical discussion of hysteresis is to be found in the section on the "Physics of Rubber" (p. 402). It is necessary at this point to go more into the condition of the materials, since this information is important in regard to test methods.

The size of the hysteresis, of course, depends on all of the circumstances which are discussed in connection with the diagram of the simple tension test (*see* p. 516 *et seq.*). Maximum hysteresis would result if the tension test were carried through to the breaking point. On the other hand, with a hysteresis test it is not necessary to be confined to any certain point on the curve. In order to avoid the danger of breaking the test piece, an upper boundary is drawn. With compounds which have a very uniform breaking value, the upper limit of the test may be placed much closer to the average breaking point than is permissible with compounds which are not uniform. Whether one chooses a definite elongation or a definite tension as the end point of the curve, makes no difference in the hysteresis test if the test is carried through only once with the same sample, but it is of importance if the hysteresis test is repeated several times with the same sample. No agreement on this point has been established as yet, since hysteresis tests are comparatively seldom carried out. Perhaps the necessity of an arbitrary choice is the reason why this test is still so little used.

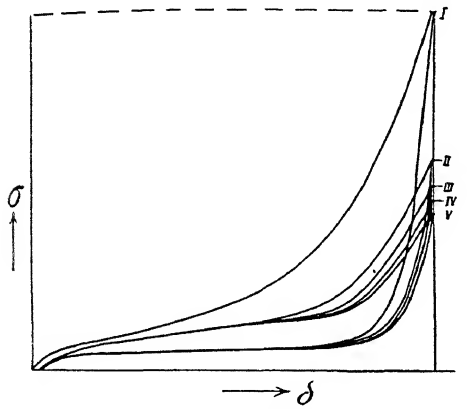


Figure 158—Repeated loading and unloading with a constant maximum elongation.

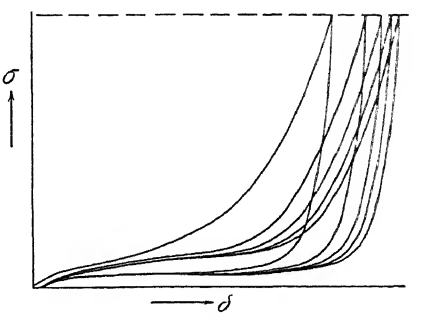


Figure 159—Repeated loading and unloading with a constant maximum tension.

In the following pages are presented a few results obtained by the Materialprüfungsamt on repeated hysteresis tests. In these tests four degrees of vulcanization of the same rubber-sulfur mix were used. These tests were carried out so that by repeated trials on one and the same sample (ring), the points of reversal of the loop in one case are at the same elongation, and at the same tension in the other. The test was carried out five times with each sample. Since the tension of the first hysteresis loop (the original curve) should be the same for all degrees of vulcanization, it had to be chosen rather low (90 kg./sq. cm. or 1,280 lbs./sq. in.) in consideration of the possibility of a break in the series with constant tension. In spite of this precaution breaks occurred in two cases after the fourth loop.

After reviewing the results as shown by eight different diagrams, it has been considered sufficient to present at this point one example (Figs. 158 and

159, which deal with the second degree of vulcanization). In both of the illustrations, Loop I is the same (within the boundaries of unavoidable inequalities of the two samples). The tension at the turning point is 90 kg./sq. cm., and the corresponding elongations are 660 and 652 per cent. On repetition, the turning point of the hysteresis loop in Figure 158 always reaches the elongation value of Loop 1 (660 per cent), and in Figure 159 it always reaches the tension value of Loop I (90 kg./sq. cm.). In Figure 158 there is a diminution of tension from loop to loop at the points of reversal, and in Figure 159 there is an increase in elongation. These progressive changes are also to be seen numerically in Table 9.

TABLE 9.—*Hysteresis Tests.*

Number of the Hysteresis Loop	Fig. 158 Maximum Tension σ_{max} Kg./sq. cm.	Fig. 159 Maximum Elongation δ_{max} per cent
I (Original Curve)	90	652
II	53	728
III	47	763
IV	43	781
V	40	797

In Table 10, the values for the areas of Loops I and V are given (without calculating the actual work values in cm. kg./cc.), expressed simply in sq. cm., since only the relation of these areas to one another (as calculated in the tables) is of importance. Furthermore, the values for σ_{max} are given for Loops IV and V for the series with constant δ_{max}, and the values for δ_{max} for Loops I, IV and V (the results of Loop IV are given, because as noted, two samples only lasted through four loops) are given for the series with constant σ_{max}.

The Impact Test

The hysteresis test may be carried out very quickly or very slowly. The testing machines available at present do not permit such high velocities that an impact effect may be obtained. The utilization of such impact effects (mainly as impact pressure stress, and not as sudden tension stress) has resulted in a great simplification in apparatus and mechanical design in regard to the determination of the hysteresis loop. The two tests depending on impact pressure action are the so-called "Falling-Ball" test, and the "Pendulum Hammer" test.

The Falling-Ball Test

The Sample as the Falling Body. The simplest method is the dropping of a ball-shaped sample of the rubber to be tested on a base which has a smooth, level, hard surface, and a considerably larger mass than the rubber ball. Here the height from which the ball has been dropped and the height to which the ball rebounds, are to be noted. The relation

$$\frac{\text{Rebound height}}{\text{Falling height}} \times 100$$

gives η_{el} directly in per cent. This simple relation is also true with the apparatus which will be discussed in the following paragraphs.

TABLE 10.—*Hysteresis Tests.*

Constant for I - V Loop	Time of vulcanization at 3 atm. min.	I Hysteresis Loop					V Hysteresis Loop				For Hysteresis Loop No.				
		δ_{max} %	A_a	A_H	A_r	η_{el} $\frac{A_r}{A_a}\times 100$ %	A_a	A_H	A_r	η_{el} $\frac{A_r}{A_a}\times 100$ %	I	IV	V	$\frac{IV}{I}\times 100$	$\frac{V}{I}\times 100$
											σ_{max}				
	10	783	27.6	20.3	7.3	26.5	13.0	8.2	4.8	37	90	52.5	50.5	58	56
	20	660	24.9	15.9	9.0	36	11.4	5.4	6.0	53	90	43	40	48	44.5
δ_{max}	40	580	23.7	12.5	11.2	47	13.0	3.9	9.1	70	90	46.5	44	52	49
	60	535	23.8	10.8	13.0	55	13.6	2.8	10.8	79	90	51.5	50	57	55.5
											δ_{max}				
	10	800	28.2	20.9	7.3	26	(23.3)	(14.8)	(8.5)	(36.5)	800	900	.....	113	.....
σ_{max}	20	652	24.5	16.2	8.3	34	21.5	11.8	9.7	45	652	781	797	120	122
= 90	40	567	22.8	12.5	10.3	45	21.1	8.5	12.6	60	567	672	685	118.5	121
kg./sq. cm.	60	540	23.8	10.9	12.9	54	(21.9)	(6.8)	(15.1)	(69)	540	633	.....	117	.....

A_a = expended energy A_r = recovered energy A_H = hysteresis energy (*see* Fig. 157)

NOTE: The values in the parentheses are taken from Loop IV since the sample broke before Loop V was completed.

The use of a rubber ball as the falling body itself, has certain disadvantages. First of all the soft rubber must be made into the shape of a ball,[46] assuming that sufficiently large pieces are available for this purpose. The second disadvantage is that the quantity of work is limited considerably by the relatively small specific gravity of the rubber ball, and in addition the weight of balls of the same diameter varies, because of the difference in specific gravity of different compounds. The use of a rubber ball as the falling body is therefore to be considered more as a rough test, which is, however, very useful as such.

Metal Balls as Falling Bodies. The objections described are avoided when a metal ball is used as the falling body and the rubber compound to be tested is used in slab form as the impact surface. Naturally, the sample must lie completely on a base of sufficiently large mass. The thickness of the sample influences the results the same way as in the ball compression test (*see* p. 556). Numerical data on the magnitude of this influence are given with the discussion of the Schob Pendulum Hammer on p. 574.

The elastometer of Pierre Breuil, built by the Cillard Company in Paris, operates according to this principle, which is also employed in the Shore Scleroscope, used in metal testing. The Elastometer "P. B.," shown in Figure 160, consists of a celluloid or glass tube (marked with graduations) which is mounted upright on the base of the apparatus. The sample in slab form is slid under the glass tube at the lower end. The tube is closed at the

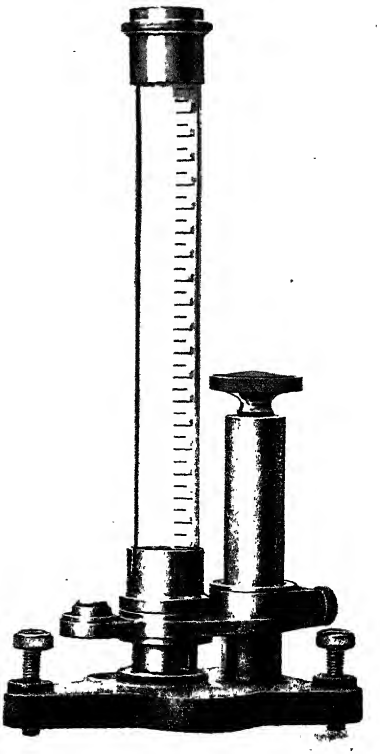


Figure 160—Elastometer "P.B.," made by A. D. Cillard, Paris.

[46] See the preparation of balls for the tests, p. 593.

upper end by a closing plate of 3 to 15 mm. diameter, which, similar to the shutter of a photographic lens, can be opened at will. When a hardened steel ball is placed on the closed upper plate and the shutter is opened, the ball drops through the tube on to the rubber slab and rebounds more or less according to the elasticity of the slab. The height to which the ball rebounds can be read from the divisions on the glass tube. The apparatus can be put into an exactly vertical position by means of three pointed screws and a level mounted on the base. Samples up to 50 mm. in thickness may be tested. Some test results which were obtained with the Elastometer are presented in Table 11.[47]

TABLE 11.—*Elasticity Tests by Pierre Breuil.*

Sample No.	Composition of compound: Rubber %	Sulfur %	Fillers %	Time of Cure: hr.	min.	Temperature of Cure ° C.	Sample thickness mm.	Elasticity test: Rebound height of ball mm.	Ratio of rebound height to falling height %
A	97	3	....	3	15	130	5.0	102	40.5
B	96	4	....				5.0	140	56.0
C	97	3	....				5.0	135	54.0
D	96	4	....				5.0	122	48.5
E	62	6	....	1	20	135	5.5	96	38.5
F	87	13	32	2	45	135	6.0	130	52.0
G	76	11	13				4.8	122	49.6
H	48	16	36	2	....	135	5.0	82	32.8
I	48	6	46	1	30	126	5.0	100	40.0
J	48	6	46				5.0	88	35.2
K	50	3	47	1	30	135	5.0	92	36.8
L	27	2	71	1	30	130	4.5	85	34.0
M	10	2	43 45	1	30	126	4.5	60	24.0

The Falling-Ball Test of Hock. The rebound of a metal ball on a rubber plate is also used as a measure of the elasticity of soft rubber, in an apparatus devised by Hock (Fig. 161). The basic difference between the device and the Elastometer of Breuil, is that the ball does not rebound vertically, but at a considerable angle from the vertical, since the rubber slab to

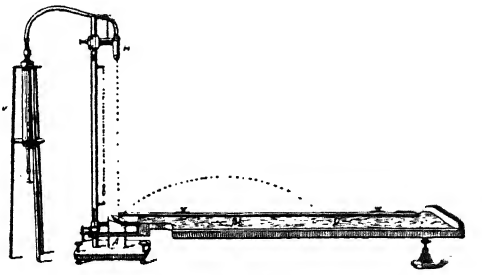


Figure 161—
Hock's elasticity tester.

be tested is placed on a slanting base. In fact, it is the horizontal distance covered by the ball which is determined, and which serves as a measure of the rebound elasticity. The rubber plate is fastened to an iron base which

[47] See *Caoutchouc & gutta-percha*, **5**, 2193 (1908).

can be set at various angles to the horizontal. On the support column, which is also mounted on the base, is a vacuum ball holder. This vacuum ball holder can be pushed up or down on the divisions provided for on the support column. The ball holder consists of a half sphere (opening facing down) to the walls of which a ball is held fast by means of suction created by an air pump through the fine opening provided at the top. When the vacuum is diminished, the ball falls perfectly, without spin or added impulse. It then rebounds from the test slab and describes a parabolic flight over the measuring board. The measuring board is covered by a sheet of paper which has a sheet of carbon paper over it. The ball in striking the board at the end of its flight, makes a mark on the paper and rolls into a runway provided for it. The distance of the striking point from the point of rebound may be measured by means of a hinged pointer which slides along the divisions of the ruler provided on the measuring board. These distances can generally be used for expressing the differences between different rubber compounds with regard to their rebound elasticities. Hock [48] recommends for very elastic samples a falling height of 50 cm., a ball 10 mm. in diameter, and the use of the base at an angle of 22.5° to the horizontal. With less elastic compounds, an angle of 10° to the horizontal should be used. An easily calibrated curve makes it possible to obtain, for a given construction of the apparatus, the relation between the measured distance of flight s, and the corresponding vertical rebound n. It is naturally of value as a measure of the impact elasticity, to determine the relation between the vertical rebound height of the ball and the original falling height h (the elastic efficiency η_{el}), which is given directly by the Breuil Elastometer. Table 12 gives a few of Hock's values for this relation, obtained with a vulcanized soft rubber compound.

TABLE 12.—*The relation between the distance covered s and the vertical rebound P* $\left(\text{that is, } \frac{100\,n}{h}\right)$ *using a height of fall H of 50 cm. and a ball 10 mm. in diameter (according to Hock).*

P	s	Angle of the base
Per cent	cm.	degrees
14.2	16.5	22.5
22.0	25.5	22.5
27.0	30.4	22.5
49.4	47.3	22.5
52.7	51.5	22.5
55.0	53.1	22.5
14.2	12.5	10
22.0	17.3	10
27.0	19.1	10
49.4	29.3	10

Hock also gives the following information in regard to the accuracy of measurements to be obtained with the apparatus:

"The recording of the distance covered by means of the carbon impression is very clear, especially when a ball 10 mm. in diameter is used. The small dots have a diameter of 2 mm. so that reading with accuracy of 1 mm. is easily possible. With greater heights of fall, the scattering that occurs, on repetition of the test, is such that the points are several millimeters from each other and an average must be taken."

[48] Hock, L., "Beiträge zur Prüfung des elastischen Verhaltens von Kautschuk, Stahl und anderen Stoffen. (Habilitationsschrift)," *Z. tech. Physik*, **6**, 50 (1925).

Since the sample is placed in a slanting position, the fall and rebound of the ball do not occur perpendicularly to the surface of the sample and part of the falling and rebound energy are changed to rotational energy, which uncontrollably influences the result, even though only in a small way.

This method of Hock's has an advantage over the method using a perpendicular rebound. With a vertical rebound, the rebound height is observed only approximately, and not very accurately, while with Hock's method the distance is actually recorded.

The Pendulum Hammer

After the war, van Itersen (Delft) and A. Schob, independently of each other, arrived at the use of the principle of the Pendulum Hammer for measuring the elasticity of soft rubber.

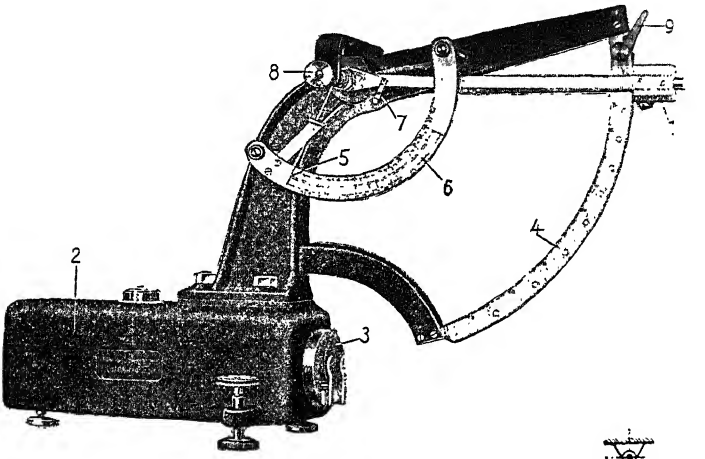


Figure 162 (Above)—Schob's impact elasticity tester (pendulum hammer).

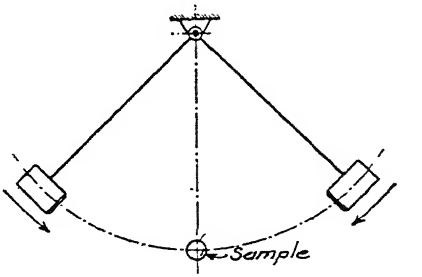


Figure 163 (Right)—Diagram of A. Schob's double pendulum system for elasticity measurements.

The Pendulum Hammer method has the following advantages over that of the Falling Ball.

1. Exact recording of the rebound height.
2. Great accuracy in reading, especially for small heights of rebound.
3. Convenient variations in regard to the size of the impact energy.
4. Possibility of making tests in swift succession (only a few seconds required for each test), so that the samples can also be tested at temperatures above room temperature without having to place the apparatus itself at these various temperatures.

The Pendulum Hammer of Schob [49] (manufactured by Schopper in Leipzig) has a maximum percussion energy of 5 cm./kg. The pendulum (*see* Fig. 162) moving in ball bearings, has a pendulum bob (1) with an impact

[49] "Ein neuer Elastizitätsprüfer für Weichgummi." *Mitt. Materialprüfungsamt, Berlin-Dahlem.* 227, 1919, J. Springer, Berlin.

weight of 200 grams. This pendulum can be moved along the arc (4) up to the latch (9) and held there. The latch can be fastened at 10 different heights along the arc (4). The maximum falling height is 25 cm. When the latch is loosened, the pendulum falls, striking against the rubber slab sample (3) which is held vertically under the pendulum axis by means of two light flat springs. The catch (7) fastened to the axis of the pendulum, catches the pointer (5) just before the impact of the pendulum on the rubber sample, and carries it to the highest point in the following rebound of the pendulum. The pointer remains at this greatest height so that the rebound height may be read from the divisions on the arc (6). The divisions on the arc (6) are expressed as percentages of the falling height, so that the elastic efficiency, that is, the relation $\frac{\text{rebound height}}{\text{falling height}}$ of the pendulum, or the relation $\frac{\text{recovered work}}{\text{expended work}}$, can be read directly in per cent of the expended energy. In order to use the pendulum with smaller falling heights; that is, with smaller impact energies,[50] the catch (9) can be fastened at 10 different heights along the arc (4) (from 1 to 1/10 of the greatest falling height H). Since the half-height is used to a great extent in practice, a second set of divisions is placed on the arc (6) for the direct reading of efficiency. If one works with other falling heights, for instance with $H' = 0.3\,H$, the reading for η_{el} on the divisions for the complete falling height is to be multiplied by the reciprocal value of the falling height used (in this case 1/0.3). The graduations on the arcs (6) and (4) are made without regard to friction or air resistance, since the losses from these latter are negligible. In spite of the careful workmanship, a small friction loss occurs in the bearings of the pendulum. Furthermore, the dragging pointer (5) must have sufficient friction so that (especially in the case of small η_{el}) the pointer is not thrown too far, and so that it fastens securely at the end position. A small energy loss also occurs when the nose of the carrier (7) passes over the pointer. These errors could be corrected by a corresponding increase in the falling height on the arc (4). Such a correction has been disregarded, however, since the whole test sample (waste strips of the normal rings used for tensile tests), which was chosen with regard for convenient and sure service, is not struck by the blow. Moreover, the results obtained are only good for comparative values (see subsequent discussion of the influences of the measurement of the sample and of the character of the surface of the sample). The errors created by friction and air resistance with the different degrees of elasticity, always amount to approximately the same fraction of the results read; that is, about 2 per cent.

To determine the design of this Pendulum Hammer, A. Schob carried out several experiments with the double pendulum arrangement shown in Figure 163, using ball-shaped rubber samples. The ball was hung on a fine thread. The two pendulums of the same mass, were then raised to equal heights and allowed to drop on the sample at the same time. By this arrangement, the rubber volume which takes up the energy of percussion, is exactly defined. The friction conditions between the samples and the impact surfaces are very

[50] Since a change in the speed of deformation occurs with the changing of the energy of fall by changing the falling height (not the mass of the pendulum), this influence should be regarded in the more accurate tests. The reproducibility of similar conditions given by the construction of the apparatus suffices for general use, when each falling height is considered by itself.

favorable, and, through the use of two pendulums, any loss of stray energy through the base of the apparatus is prevented. Physically, therefore, this method is without objections. Because of practical considerations, the previously described form of the Pendulum Hammer was chosen, however.

It is important to keep the errors in the apparatus constant in order that comparisons between different apparatus in different places can be made. The limit of error previously specified can be maintained if the frictional resistance of the pointer (5), measured on its outermost point, is approximately 3 grams, and the resistance required to push back the nose of the carrier (7), is approximately 60 grams. The lower resting position of the pendulum (1), when it is allowed to come into this position very slowly, once from the left and once from the right, should not show a difference of more than 0.5 mm., measured at the lowest point. It is advisable to check the friction of the pointer (5) from time to time, by placing the pointer in a horizontal position and hanging a 3 gram weight on the end. The pointer should drop smoothly under this loading. The necessary spring tension of the carrier (7) is properly chosen during the construction of the apparatus, and it is only when a damaged spring must be replaced that any attention must be paid to it.

As a consequence of the impact of the pendulum, the anvil is given a little motion, which it in turn transfers to its base. In order to determine the effect of the method of support the apparatus was set up the first time on rollers, so that it could easily move in the direction of the impact, the second time on a solid table of medium size, and the third time on a solid floor. All three experiments were carried out, using the full falling height ($H' = 1.0\,H$), with a soft, very elastic material and also with a very inelastic material.[51] All the conditions were otherwise the same. With both materials the highest values were obtained with the freely moving apparatus, and the lowest with the apparatus placed on the solid floor. Corresponding to the slight yielding of the table, the values when this arrangement was used lie between those for the other two.[52] For all the following tests mentioned, the apparatus was placed upon that same table.

It was to be expected that the surface of the test sample would be of considerable influence upon the test results. For determining the errors of the apparatus, the same sample was always used. It was thus possible to eliminate all the differences which are possible in the material itself, and which would obscure the results. A large series of tests showed that by repeated blows upon the same sample (with exceptions which do not come into consideration here) there is an increase in the values of η_{el}, which disappears again, however, after a short rest. In tests in further series the initial values were always obtained again. A slab, 6.0 mm. thick, of mechanically milled, high-grade automobile inner-tube compound, used in block form, was used for the tests listed in Table 13.

The different conditions of the surface of the sample are to be seen from the table. The figures for η_{el}, written one under the other, give the readings of direct successive blows. The increase in η_{el} with successive blows, which is barely noticeable in the first two columns only, becomes clearly

[51] These tests were carried out during the war at the time of the greatest rubber shortage. This accounts for the selection of the test materials.

[52] This first striking phenomenon is explained by the rigid connection of the pendulum axis with the anvil. With the freely moving setup of the apparatus, the pendulum bearing participates in the movement of the anvil which is directed against the rebounding pendulum so that an increase in the rebound height results.

TABLE 13.—*The Influence of the Surface of the Sample Upon the Results of the Test.*
Total Falling Height ($H' = 1.0\ H$)
Material: Mechanically Worked Red Automobile Inner Tube Stock

	Values for the elastic efficiency, η_{el}[b]				
(1)	(2)	(3)	(4)	(5)	(6)
53	45	48	47	48	45.5
54	45.5	48	47	48	45.5
54	45.5	48	47	48	45.5
54	45.5	48	47	48	45.5
54	45.5	48	47	48	45.5

(1) Both sides carefully rubbed the day before with alcohol-benzine (surface of entirely clean rubber).[a]
(2) Both sides rubbed with talcum.
(3) Both sides rubbed with talcum, and the talcum rubbed off as clean as possible with a dry cloth.[a]
(4) The hammer side of the sample again rubbed with talcum.
(5) The hammer and hammer side of the sample rubbed off dry again, and the anvil side of the sample rubbed with talcum.
(6) Both sides of the sample rubbed with talcum again.

a The surfaces of the hammer and the anvil well cleaned.
b The numbers in the columns are the values for immediately succeeding blows.

evident under slightly different conditions. The greatest values (Column 1) are obtained with an entirely clean surface. The values for η_{el} are lowered the most when both sides of the sample have been rubbed with talcum (Column 2). Vigorous rubbing with a clean cloth allows the value to rise again to not quite one-half of the difference (Column 3). After the sample was subjected to the treatment given in columns 4 and 5, it was again rubbed on both sides with talcum. The same values were obtained in column 6, as had been obtained in column 2. The rubbing with talcum is performed by using a cotton wad, or more simply with the dry finger tips. The excess talcum is knocked or lightly blown off. It is shown in Table 13 that uniform values are obtained by rubbing the sample with talcum. Varying the amount of talcum rubbed on (within fairly wide limits) is of no importance, since very slight contamination of the surface (Column 3) results in essentially different values from those of an entirely clean surface. It is exceedingly hard and inconvenient to produce and to maintain an entirely clean surface, especially since the test pieces are to be cured in sheets of the proper thickness (6 mm.) and are not cut out of full blocks. It is, therefore, advisable to carry out tests with the Pendulum Hammer with samples which have been rubbed on both sides with talcum.

Another series of comparisons is presented in Table 14. Use is made of a harder material (red carriage tires), with very clean test surfaces, and surfaces rubbed with talcum. In Table 14 are also to be found (especially with the thinner samples) appreciable differences, which diminish with increase in sample thickness.

The main reason for obtaining the results shown in Table 14 was to determine the influence of sample dimensions on the elastic efficiency. Samples with different thicknesses, from 15 to 44.6 mm., as well as from 2 to 10 mm., were used. The numerical values in Table 14 are placed together as graphs in Figure 164. In order to make possible the representation in a coordinate system of two axes, in spite of the three existing variables (η_{el}, width and thickness), the different thicknesses of sample are distinguished by different signs, as explained below the figure. The values clearly show that, within the chosen limits, the diameter of the sample exerts no influence, but that η_{el}

TABLE 14.—*The Effect of Different Thicknesses and Diameters of the Sample Upon the Results of the Test.*
(Total Falling Height Used)
Material: Red Carriage Tire.

Sample dimensions		Elastic efficiency η_{el}*	
Diameter d mm.	Thickness s. mm.	Without talcum	Per cent With talcum
44.6	10.0	49.5	49.5
36.6	10.0	50	49.5
	7.8	47	46
	6.1	46	42
	2.5	32	23.5
25.0	10.0	49	49
	7.7	47.5	47
	5.6	44	41.5
	1.8	22	14.5
20.0	10.0	51.5	50.5
	7.8	48	47
	6.0	44.5	42
	2.8	33	23.5
	1.9	22	14
15.0	10.0	49	48.5
	7.8	48	46.5
	6.7	46	43
	3.8	39	32
	3.2	35.5	28
	2.0	25	18
	1.5	17	10.5

* The values given here are the values obtained from the last of five successive blows upon the same sample.

decreases greatly with a decrease in sample thickness. These results made it necessary to make further tests with samples of varying thicknesses but constant diameter.

As was to be expected, different falling heights of the hammer also had a distinguishable influence on the results. The experiments involving variation in falling height were carried out by using 4 materials having sample thickness between 4 and 7 mm., and by employing falling heights of $H' = 0.1$, 0.2, 0.5 and 1.0 H. The smallest fall was used first since in the reversed case results would be affected by the influences of the preceding stresses while the influences of smaller preceding stresses would have no effect on the succeeding results. Only the results obtained with the first of the five successive blows was used for the drawing of the illustrations, one of which is presented in Figure 165.

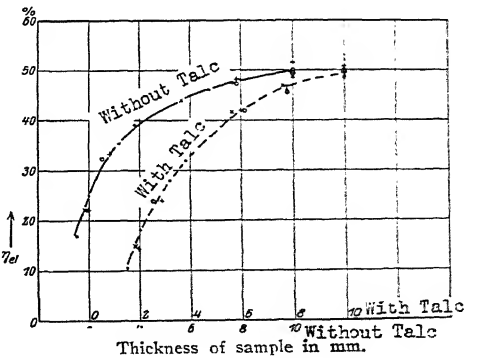


Figure 164—The effect of the thickness of sample upon the elastic efficiency η_{el}.

● = 15 mm. sample thickness.
+ = 20 mm. sample thickness.
× = 25 mm. sample thickness.
○ = 36.6 mm. sample thickness.
△ = 44.6 mm. sample thickness.

Tests were also carried out with the same sample, with the temperatures varying from approximately 0° C. to 45° C. and with one blow from the full falling height. Figure 166 gives the results for material "a." To test the

effect of temperature variations, the samples were stored for a long time in receptacles which were kept at these temperatures; then taken out quickly and tested. The time which elapsed between removal from the receptacle and the blow, was limited to 4 or 5 seconds, so that with temperatures which did not deviate too greatly from the room temperature, no mentionable deviation of the actual temperature of the sample from the theoretical temperature could have occurred. In the planning of the apparatus, consideration was given to the possibility of providing for the execution of tests at higher and lower temperatures by enclosing the whole apparatus and operating from the outside. For most cases in practice (for which the apparatus was primarily designed) these complications of the apparatus are unnecessary.

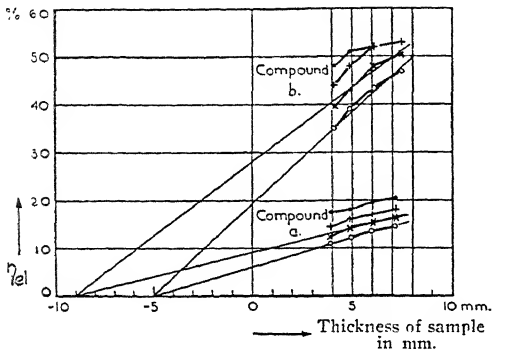


Figure 165—The effect of variation in the thickness of the sample and in the height of fall of the pendulum upon the elastic efficiency η_{el}.
O = 1.0 H (complete falling height).
× = 0.5 H.

H.

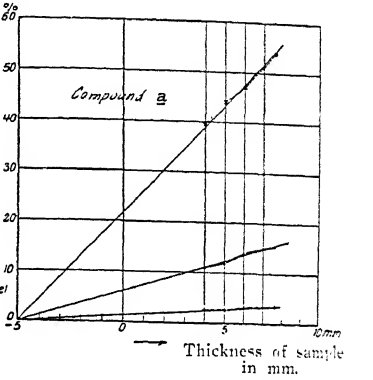


Figure 166—The effect of temperatures upon the elastic efficiency η_{el}, with the complete falling height and various sample thicknesses.
Upper line: 45° test temperature.
Middle line: 22° test temperature.
Bottom line: 0° test temperature.

In common with the curves of Figure 164, those of Figures 165 and 166 show the dependence of elastic efficiency η_{el} on the thicknesses of sample. The curves for the higher values of η_{el} rise steeply at first; then slowly become flatter. A thickness of 6 mm. has been considered as the normal thickness of sample. It corresponds to the normal thickness of the strips used for tension tests in the Schopper-Dalén machine. This value is not always obtained in the preparation of the slabs. If test strips with thickness greater or less than 6 mm. must be tested, the readings should be corrected to the 6 mm. thickness. In considering the curves in Figures 165 and 166 for the full height H, the bent portion of the curve lying between thicknesses of sample of 5 mm. and 7 mm. can be straightened out into a straight line which has sufficient accuracy for practical purposes. With the different materials and temperature variations, the straightened line for a sample of thickness between 5 mm. and 7 mm. crosses the horizontal axis at — 5 mm. It was found that when the value of η_{el} determined with a sample of thickness between 5 and 7 mm. was multiplied by $\frac{11}{S+5}$ (in which S denotes the sample thickness) the value for η_{el} obtained was exactly the same as when using a

sample exactly 6 mm. thick. With a falling height of $H' = 0.5\ H$ (Fig. 165), the point where the extended curve crosses the horizontal axis is at — 9 mm. for sample thicknesses between 5 and 7 mm. The correction factor in this case is $\frac{15}{S+9}$.

The values of η_{el} for a 6 mm. sample thickness and the total height of fall, are plotted in Figure 167 as a function of the temperature of the experiment. From these curves it is apparent that the elastic efficiency of Methyl rubber (*a*) as well as that of natural rubber (*b, c, d*) is greatly influenced by a temperature variation of as little as 1° C., the efficiency increasing with temperature. This conclusion was confirmed by the results of other experiments not reported here. The opposite curvatures in the cases of Methyl rubber (*a*) and of natural rubber (*b, c, d*) show that the exact manner of variation with these rubbers is different. A definite testing temperature should be set; best of all 20° C. Otherwise uniform results cannot be obtained. In certain cases, varying test temperatures can naturally offer special interest.

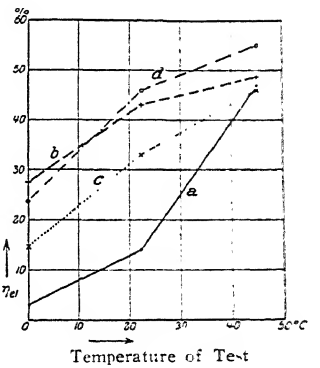


Figure 167—The dependence of the elastic efficiency η_{el} on the temperature of the experiment in the case of four different materials (a, methyl rubber compound; b, c and d, natural rubber compounds).

The data show that with determinations of elasticity of soft rubber, just as with all other testing results (tension, compression, hardness, crushing, etc.), exact agreement on sample shapes, etc., is necessary if comparative results are to be obtained.

The summary, based on the experimental results discussed in the work with the impact elasticity tester of Schob's construction, is as follows:

As a rule, the strip stamped out of the soft rubber sheet for normal tension tests; that is, a strip 6 mm. in thickness and 44 or 36 mm. in width, is to be used as the test sample. The diameter may vary through wide limits, but the thickness of strip has an important influence on the test results. With strips between 5 and 7 mm. in thickness, the readings for η_{el}, working with the pendulum at the full height, are to be multiplied by $\frac{11}{(S = \text{strip thickness})}$ in order to obtain the comparative values for a sample exactly 6 mm. in thickness. Operating at the half-height, the readings are to be multiplied by $\frac{15}{S+9}$

The samples should be carefully rubbed with talcum before the test, because the surface condition influences the test results. Furthermore, because of the great dependence of the elasticity of soft rubber on the temperature, the test temperature of 20° C. should be maintained as exactly as possible.

The Determination of the Degree of Plasticity

General Notes on Plasticity

Plasticity may be contrasted with elasticity. It should therefore be discussed in conjunction with the section on elasticity, even though it is used primarily in connection with uncured rubber, while the testing procedures already discussed are used (in practice at least) almost exclusively with cured compounds. There is naturally nothing to prevent the use of these methods on uncured rubber, although such a use gives information largely of scientific interest only.[53]

A plastic substance is one which on being deformed by an external force, retains its new shape, even after the effect of the external force has been removed. The obvious contrast to elasticity can only be expressed in the test methods by the elongation set δ' of the tension test (p. 561) and of the hysteresis experiments (p. 564, Fig. 157). The previously discussed limitations with respect to elongation set again apply; i.e., the elongation set is generally a function of time, and is also affected by the "elastic after-effect." Temperature influences are also important. Only the actual permanent portion of the elongation set represents the pure plastic deformation.

Although hysteresis measurements are of value for the determination of elastic behavior, they do not serve as well as a measure for plasticity, since the hysteresis loss in the case of plastic materials is not at all confined to the work of deformation, but also includes an energy change of another kind which accompanies deformation. In practice, the amount of work necessary for a non-elastic deformation is important (for instance, in the milling of crude rubber and rubber mixtures) but it can not be used as a measure of plasticity, which is defined in terms of the magnitude of deformation (linear).

The size of the deformation (elongation with tension tests and compression with compression tests) which remains after the external forces have been removed, is accordingly used as a measure of plasticity. Because of the unusually great capacity for plastic deformation exhibited by soft rubber, it is of interest in most cases to consider the plastic deformation not only for itself, but also with respect to the total deformation or to the elastic deformation.

Experimental Methods

Extrusion Method

Marzetti's[54] method for the determination of plasticity is used as a control on the mixing and vulcanizing of rubber compounds. The masticated rubber is forced through an orifice by means of air pressure, and the rubber strand which has been forced through after a certain length of time, is measured or weighed. After each interval, the rubber strand is notched by means of a knife fastened at the opening. On the left in Figure 168 is shown the apparatus, which requires no further explanation, and on the right are two strands of rubber, each notched at 15 minute intervals. The upper end of the left-hand strand shows a shortening in sections, indicating curing or "setting-up" of the stock. The experiment may be carried out at different temperatures without difficulties, by placing the apparatus in a glycerine bath. The knife U which is used to make the notches, can be operated by means of the lever L which extends out of the bath.

[53] See Rosbaud, P. and Schmid, E., *Z. tech. Physik*, **9**, 98-106 (1928).

[54] *Giorn. chim. ind. applicata*, **5**, 342 (1923) and *India Rubber J.*, **66**, 417 (1923).

J. Behre* [*Kautschuk*, **8**, 2, 167 (1932)] has recently discussed the results of seven years' work with a plastometer of the Marzetti type. He found that it gave results which agreed well with those obtained during practical mill, calender, and tubing machine operations, and concluded that it provides a more certain indication of the behavior of raw rubber and rubber stocks than do parallel-plate plastometers in general.

The most recent development in connection with extrusion plastometers is that covered in a paper by J. H. Dillon and N. Johnston [*Physics*, **4**, 225 (1933)]. In contrast to those used by Marzetti and others, the plastometer of Dillon and Johnston operates at rates of shear comparable with those employed in factory tubing machines. This plastometer consists essentially of a hardened steel piston which extrudes the rubber through a die at the lower end of a steel cylinder. The piston, which is 0.5 inch (1.27 cm.) in diameter, is operated through a distance of 3 inches (7.62 cm.) by a pneumatic piston having a diameter of 5.5 inches (13.97 cm.). Thus, the air pressures of 5 to 80 pounds per square inch used in the pneumatic cylinder, correspond to 605 to 9680 pounds per square inch pressure exerted on the rubber. For further details regarding the plastometer, the reader is referred to the original article. The relation between rate of efflux and pressure was measured for various types of rubber stocks with this machine. This relation was found to be very different for pure gum stocks as compared to highly compounded stocks, such as those used for the treads of pneumatic tires. The results obtained with this extrusion plastometer have been compared with those obtained with the Williams instrument, and a possible explanation of the partial failure of the compression-type plastometer to correlate with factory extrusion machines is presented in the original paper.

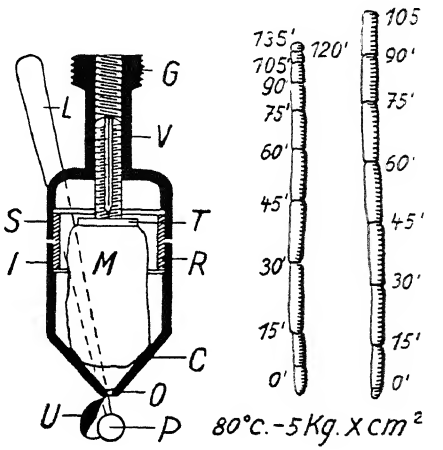


Figure 168—The Marzetti apparatus for plasticity measurements.

Other Methods

Williams, de Vries, Griffith and van Rossem used the compression of a measured amount of rubber under a certain weight, or the impression of a punch piston, as the measure of plasticity. This method can be used for crude rubber, masticated mixtures and vulcanized rubber, at different temperatures, without any difficulty.

The simple construction of the apparatus of these authors is essentially the same. A picture of one such apparatus, namely that of de Vries and van Rossem, appears in Figure 169, while that of Williams (much used in America) is shown in Figure 169a. In the apparatus first mentioned, a measured amount of rubber is first compressed between the two smooth plates under a definite loading. In order to obtain clearly visible conditions, van Rossem fastened a punch, 1 sq. cm. in area, in the center of the bottom plate.

* Translator's note by V. N. M.

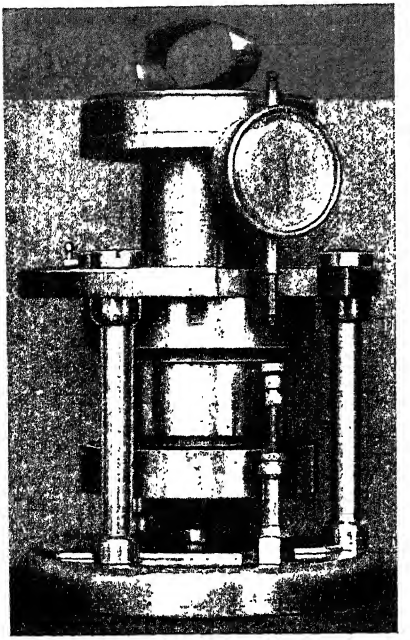


Figure 169—The Plastometer of de Vries and van Rossem.

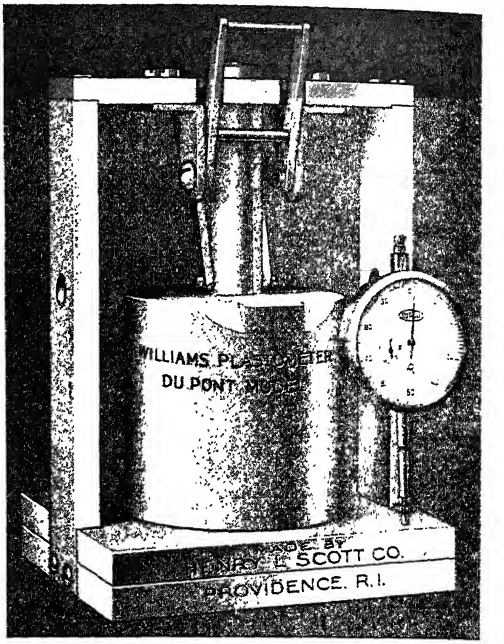


Figure 169a—The Plastometer of Williams.

The depth of penetration of this punch in the rubber, under the influence of a 5 kg. loading weight, is equal to the lowering of the weight. This lowering is measured on a gauge, which is graduated to 1/100 mm. Van Rossem,[55] in a lecture based on the joint experiments carried out with van der Meyden and earlier work, discussed the different effects observed during the use of the plastometer. The total compression which the apparatus indicates is partly plastic and partly elastic. The elastic portion is also strongly under the influence of the so-called "elastic after-effect." The size of the elastic and plastic portions depends greatly upon the temperature.

The values given here were taken from this lecture by van Rossem. In Figure 170 are presented curves (obtained at different temperatures) which show the decrease in height of the experimental samples of masticated crude rubber, under equal loading in the plastometer, in relation to the loading time. If the samples are released after a definite length of time, the division into the purely plastic deformation and into the elastic after-effect may be followed from the magnitude and the speed of the decreasing deformation. Since the graph for this is not so clear, the corresponding tables from van Rossem's work are also given here (Table 15).

The figures in the first column show that the deformation suffered during the loading is purely elastic, although the elastic after-effect lasts two hours. In column 2 a considerable portion of the deformation is truly plastic, although a considerable elastic after-effect is still present. In column 3, the plastic portion of the deformation is in preponderance by far, and the elastic after-effect is very small.

[55] International Congress for Testing Materials, Amsterdam, **1927**, Vol. II, p. 479, Martinus Nijhoff, The Hague, **1928**. See also *Kautschuk*, **3**, 369 (1927).

TABLE 15.—*The Behavior of Masticated Crude Rubber After Release in a Plastometer (According to A. van Rossem and H. van der Meyden).*

(The Thickness of the Samples Expressed in Hundredths of a Millimeter.)

Temperature of the test:	16° C.		45° C.		70° C.	
Original thickness of the sample:	210		218		190	
Pressed in the Plastometer to:	115		44		17	
After	1 Minute	130	After 1 Minute	46	After 1 Minute	22
" 5	"	155	" 3 "	57	" 7 "	27
" 10	"	173	" 8 "	64	" 20 "	27
" 15	"	178	" 13 "	71	" 30 "	28
" 20	"	183	" 18 "	80	" 90 "	30
" 25	"	189	" 23 "	84	" 150 "	32
" 30	"	192	" 28 "	86	" 180 "	32
" 40	"	197	" 95 "	115	" 270 "	33
" 45	"	198	" 108 "	117	" 330 "	33
" 50	"	199	" 120 "	119	" 24 Hours	35
" 60	"	201	" 150 "	123	" 72 "	35
" 65	"	202	" 210 "	125		
" 80	"	205	" 240 "	126		
" 90	"	207	" 300 "	127		
" 110	"	209				
" 120	"	210				

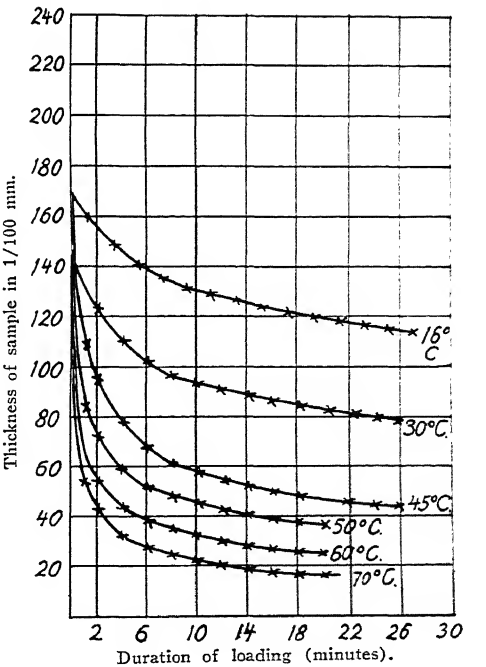


Figure 170—The relation between the plastometer readings (ordinates) and the duration of loading, at various temperatures (as found by van Rossem and van der Meyden).

Figure 171 shows the dependence of the plastometer indication on the time, for rubber with several different degrees of vulcanization, using an experimental temperature of 147° C.

The influence of the temperature of test in the determination of the plasticity of vulcanized rubber (92.5 per cent crepe and 7.5 per cent sulfur) is

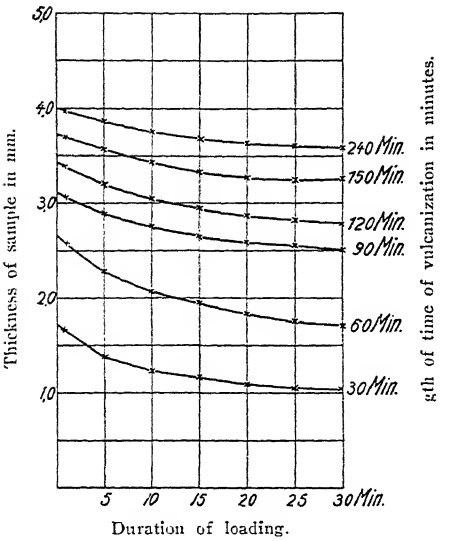


Figure 171—The dependence of the plastometer readings (ordinates) on the duration of loading and on the degree of vulcanization of the compounds, at a temperature of 147° C. (as found by van Rossem and van der Meyden).

to be seen in Table 16. In this table are shown the portion of elastic recovery from compression (the purely elastic part) which is to be noticed immediately after release of loading, the elastic after-effect, and the purely plastic portion (corresponding to the remaining compression) in per cent of the total compression, without regard to its absolute magnitude.

TABLE 16.—*The Influence of the Temperature of Testing Upon the Measurements Taken with a Plastometer.*

(According to A. van Rossem and H. van der Meyden.)

Testing temperature ° C.	Duration of vulcanization min.	Purely elastic portion %	Elastic after-effect %	Purely plastic portion (Residual compression) %
18	30	59	37	4
	60	81	19	0
	90	89	11	0
	120	93	7	0
	150	100	0	0
	240	100	0	0
100	30	62	18	20
	60	85	15	0
	90	95	5	0
	120	94	6	0
	150	93	7	0
	240	100	0	0
130	30	23	53	24
	60	71	14	15
	120	75	23	2
	240	92	8	0
147	30	21	25	54
	60	38	24	38
	90	45	32	23
	120	55	18	27
	150	61	16	23
	240	65	7	28

The B. F. Goodrich Company* [Karrer, E., Davies, J. M., Dieterich, E. O., *Ind. Eng. Chem., Anal. Ed.*, **2**, 96 (1930)] has developed a plastometer which operates on the principle that plasticity is a function of softness and retentivity of deformation. In this plastometer, a cylindrical sample 1 cm. long and 1 sq. cm. in cross section, is placed between two vertical rods which have a cross-sectional area of 1 sq. cm. The original height of the sample is taken, a definite load is applied to the sample through the upper plunger for a certain length of time, and the height of the sample is again recorded. The load is then removed and the height of the sample is again recorded after a definite length of time. Plasticity is then calculated, using the value of the force applied, the length of time of application, the original height of the sample, the height under compression, and the height after recovery. This plastometer operates rapidly and gives consistent results.

G. W. Usherwood [*Trans. Inst. Rubber Ind.*, **8**, 227 (1932)] has described a plastometer, which was developed in England, and which is somewhat similar in design to the modified Goodrich plastometer discussed above.

Protracted Tests

The designation "Protracted Tests" in material testing is neither fortunate nor clear. This expression denotes—

(a) Experiments in which a test sample is subjected to an oscillating stress, with many repeated changes, with increasing and decreasing tension within definite tension or deformation limits, or—

(b) Tests in which a protracted action of a constant loading or deformation occurs.

In both cases, the amount of loading or deformation employed does not reach the breaking value which may be found in the case of a simple test of strength with a single stressing or deformation at break.

The English word "fatigue," refers, preponderantly if not entirely, to the first group; that is, to oscillating stressing. This conception of "fatigue" is also conveyed by the word "Ermüdung" often found in the German literature on materials testing, although it is doubtful whether a material change analogous to physiological tiring is the cause of breaks which, in the case of repeated stressings, are found to occur far under the usual breaking tension.

The word "endurance," used in the English technical literature, refers more correctly to the properties of materials in question, but "endurance tests" sound a bit unusual. "Durability" also covers the idea, but goes further, since by it is also understood the resistance to change of material properties following the so-called "aging." The term "protracted break," if used for a break caused by protracted stressing would be literally wrong, for the break always "lasts," whether it be caused by a single or a repeated stress.

The same kind of stresses used for the ordinary short-time tests can be applied to the long-lasting tests with constant stress. Consideration is to be given to the following types of stress: tension, compression, shear, bending, kinking, twisting, and combinations thereof. With repeated or oscillating stress, further possibilities of combination exist, especially as a consequence of the reversal of the direction of the stress with each oscillation. Alternating tension and compression may result for instance.

Tension stressing is the most interesting of all the methods of stressing. In spite of the fact that repeated tension stressings are important in soft rubber testing (the importance can be also seen from the hysteresis illustrations in Figs. 158 and 159) such tests have been carried out very little as yet. Perhaps the main reason for this is the great cost of such tests, if they are

* Translator's note by E. O. E.

carried out somewhat systematically; that is, if consideration is given to the many possibilities of variation in regard to the size and frequency of the stress, as well as to the different temperature variations. As was mentioned in the explanation of the hysteresis curve, there are no preferred points in the soft rubber diagram, which can serve as a basis for the choice of stresses for repeated stressings. In addition, there are secondary effects which occur with the tests of long duration, which will not be discussed here. The most important secondary effect, natural aging, is influenced by mechanical working.

The first apparatus built for testing with repeated stresses, was the combination rubber tester of P. Breuil's, made by the Cillard Company in Paris (described on p. 549).

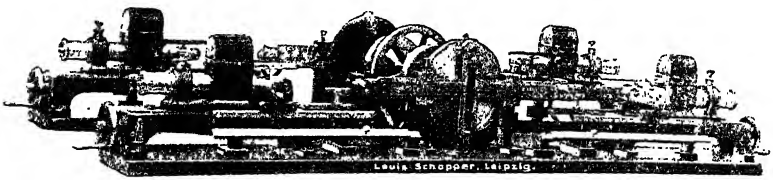


Figure 172—The Martens-Schopper protracted test machine.

The Materialprüfungsamt uses the Martens-Schopper apparatus (shown in Fig. 172), which permits the simultaneous stretching and release from tension of four normal rings (individual adjustments for each ring). The amount of tension is measured by helical springs. The clamping device for the ring samples is similar to that of the rubber tester of Schopper-Dalén (*see* p. 542). The rings travel over the clamping rolls during the lengthening and shortening. Counting devices, which automatically cease operating when the samples break, show the number of changes in stress. If the elongation set is to be measured after a certain number of stressings, the elongation measuring device of Martens-Schopper (described on p. 563) is used. A few of the results obtained with this "fatigue"-testing machine, are given in Table 17.

A protracted test* developed and used by the Firestone Tire and Rubber Company [Cooper, L. V., *Ind. Eng. Chem., Anal. Ed.*, **2**, 391 (1930)] tests the flex-cracking resistance of any stock from which a dumb-bell strip may be cut. This machine subjects rubber stocks to repeated elongation, producing flex cracks which are very much like those received in actual flexing service. In this test dumb-bell strips are fastened to two horizontal beams, the lower one being stationary and the upper oscillating vertically. During each oscillation of the upper beam the sample is stretched from zero per cent to a definite elongation which may be regulated. This machine is small and compact and may be mounted in the sunlight or enclosed so that samples may be tested at elevated temperatures or surrounded by an atmosphere of a gas other than air.

The back-and-forth bending tests, the simplest method of execution of which is illustrated in Figure 173, are also convenient to use. Considered from the standpoint of material testing technique, they belong to the so-called technological tests, under which are included those tests in which definite deformations are obtained (it does not matter whether it is a single or repeated stress) without the necessity of measuring the forces required to obtain these deformations. The bending radius in the back-and-forth bend-

* Translator's note by E. O. E.

TABLE 17.—*Experiments by Martens with Repeated Stretching of Soft Rubber.*

No. of the Material	Material	Maximum elongation in the protracted test per cent	The average of the load reversals until break, taken from 3 parallel tests ΣA_m	Variation of the individual values of ΣA when $\Sigma A_m = 100$	Remarks
1	Para + 10% S cured properly	86 86 86	130,300	117 92 91	Wearing occurred on the inner surface during the test.
2	The same 25% undercured	87 87 87	156,050	68 129 103	Excessive wearing on the inside. Several cracks appeared on the outside before the actual break occurred.
3	The same 25% overcured	86 86 86	96,310	81 73 146	No wearing. Cracks on the inside.
4	The same 50% overcured	86 86 86	60,980	126 102 74	No wearing. Cracks on the outside.

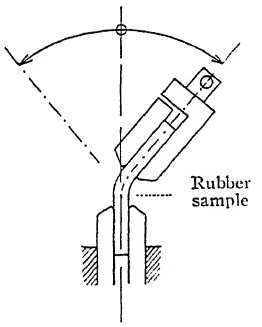


Figure 173 (Above)—The plan of the simple back-and-forth bending test.

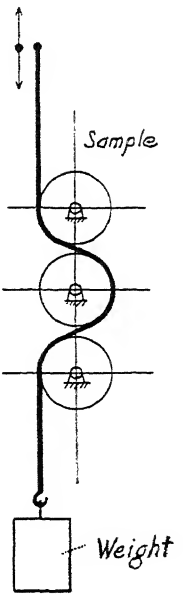


Figure 174—A back-and-forth bending test over rolls.

ing test shown in Figure 173 is not definite. If a certain bending radius is to be maintained, the test method shown in Figure 174 may be employed. In this test, the sample, in band or cord form, is pulled back and forth over rolls, while under a definite tension.

Among machines of this type developed in America* are the duPont machine [*See* A. M. Neal and A. J. Northam, *Ind. Eng. Chem.*, **23,** 1449 (1931)] and that of P. M. Torrance and L. C. Peterson, [*India Rubber World,* **80,** No. 4, 62 (1929)]. In the case of the duPont machine, a belt comprised of molded rubber links backed with cord fabric is flexed over a series of pulleys. The failure of the sample is indicated by the appearance of small nicks which soon increase in size until they become deep cracks often extending all the way across the test piece. The flexing apparatus is inclosed in a case provided with an air-tight glass front. It is thus possible to flex the belt in any gas medium desired.

The machine of Torrance and Peterson was designed especially for the study of the cracking of tread stocks. It consists of a rotor disk one inch thick, keyed to the shaft of a 1/4 h. p. induction motor, and radially slotted about its periphery so as to take twelve samples. Around this rotor is a steel ring placed off center with respect to the rotor. The test samples are mold-cured slabs of rubber, 1 x 1⅛ x $\frac{5}{16}$ inch, having two semi-circular grooves molded across their width. As the rotor turns, the test pieces are flexed through a 90° angle as they pass that point on the ring closest to the rotor and are straightened out again at the opposite side of the ring. Since the motor operates at approximately 1,725 r. p. m., the samples are flexed 2,484,000 times in 24 hours, which is sufficient time to develop serious cracking in a tread stock not containing an antioxidant effective in imparting resistance to flexing. This machine is reported to sults which check qualitatively with those of road tests.

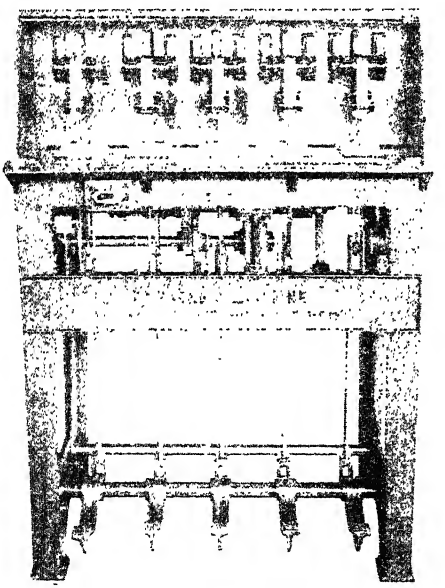


Figure 174a—Flexing machine developed by the United States Rubber Company.

A protracted test which evaluates the flexing life of rubber goods which are composed of rubber and fabric, has been developed by the United States Rubber Company.† [Gibbons, W. A., *Ind. Eng. Chem., Anal. Ed.,* **2,** 99 (1930).] In this test a strip of the sample composed of several plies of fabric and rubber is bent around a hub until its two faces are nearly parallel (*See* Fig. 174a). A weight is applied to the hub so that the strip is pulled taut. The jaws which hold the ends of the strip are moved reciprocally so that the strip drives the hub and is moved back and forth around the hub. This is continued until separation occurs between the plies of the strip. This test is used extensively to evaluate tire carcass stocks and belting.

* Translator's note by V. N. M.

† Translator's note by E. O. E.

The long-duration tests with a constant stress, in which the size of the load or of the deformation is kept constant, can be conducted without complicated apparatus. Both are used in practice, although preference is given to the simpler one; that is, the one with constant deformation, in which the effective forces are not measured. The stretching tests for the determination of elasticity described on p. 561 belong to this type. The durations of stretching are so short, however, that these tests cannot be classed as "protracted" tests. Rubber also changes its mechanical properties without being stressed; that is, it "ages." This aging, which is dealt with more thoroughly in a later section (*see* p. 604), exerts an influence in long-lasting mechanical stressing. It will even be accelerated and will finally become the main factor. It is impossible to observe the influence of each factor separately, and therefore long-duration, constant stressing is used to assist the "aging."

In order to subject rubber rings (the waste rings which are obtained from the outside scrap produced during the ring stamping may be conveniently used) at constant tension to natural as well as artificial aging (*see* p. 617), A. Martens [56] stretched them upon a glass plate, which was approximately 8 mm. thick and which had rounded edges (as is shown in Fig. 175). O. de Vries conducted aging tests in a similar manner at a later date.

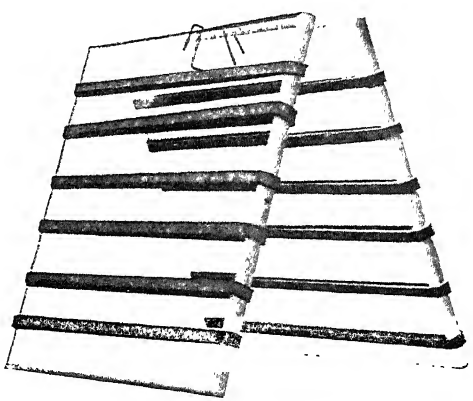


Figure 175—Aging samples stretched over a glass plate.

(According to method of A. Martens).

At the suggestion of A. Martens, experiments were also carried out in the Materialprüfungsamt, using constant loading over a long period of time and employing the arrangement shown in Figure 176. The load was very small, the original value of 1 kg./sq. cm. being raised to 1.5 and finally to 2 kg./sq. cm. The observed variations of elongation with time are shown in Figure 177. During the first 175 days the load was repeatedly released for several days, as is shown in the diagram.

In practice, compression is the only test besides tension which is used for long-duration tests with constant stress. The clamping devices for this test are also of the simplest kind.

Several instruments for protracted compression and compression set tests, which are especially adapted for the testing of rubber automotive equipment, have been developed in the laboratories of the Firestone Tire and Rubber Company.* [Abbott, F. D., *Ind.*

[56] Martens, A., "Über die technische Prüfung des Kautschuks und der Ballonstoffe im Kgl. Materialprüfungsamt," *Sitzber. preuss. Akad. Wiss.*, 14 (1911).

* Translator's note by E. O. E.

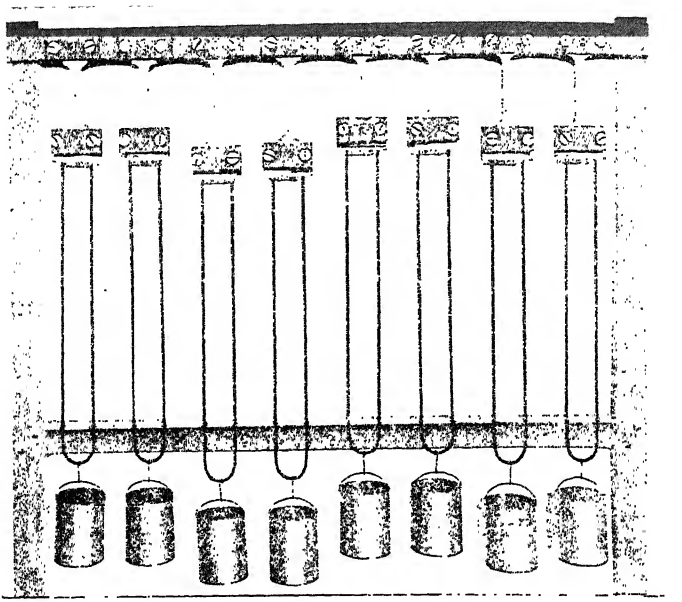


Figure 176—Protracted tension tests with constant loadings.

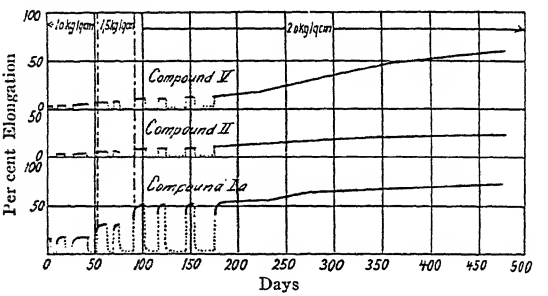


Figure 177—Long duration tests using very small loads, interrupted by long resting periods.

Eng. Chem., Anal. Ed., **2**, 145 (1930).] One instrument, the compressetometer, is useful in making deflection, hysteresis and set tests under constant load or constant distortion. This instrument applies compressive loads to test pieces by means of three tension springs. By turning a hand wheel the springs are made to pull a plunger down on to a sample resting on the bottom plate. The loads are measured on a scale and a gage measures the deflections. The test samples are small round discs.

An instrument to make compression set tests under constant distortion consists of two parallel steel plates clamped together by means of four bolts passing through the plates near the corners. A compression set clamp with which tests can be made at constant load, consists of two parallel steel plates with long tie bolts, and a short compressive spring inserted between the plates. The sample is placed on a steel disc on top of the spring and is loaded by compression of the spring. The last instrument is used primarily for permanent set testing.

Crushing Tests

General Terms

The crushing tests occupy a special position among soft rubber test methods. The stressing of the rubber sample (ball) during this test is very complicated. From the standpoint of the main stress which works externally upon the ball, the crushing test can be considered as a repeated compression test in which the line of direction of the compression forces is constantly changing because of the rotation of the ball. In order that crushing and not external abrasion may occur, the loading of the ball must be chosen high enough so that the test is completed in a few hours. This cannot be called a long-duration test, even though it is a test with repeated (oscillating) stressings, and one in which the direction of stress is alternating. In all oscillatory stressing, the work of deformation (which plays a rather insignificant part in the case of tests with a single loading) is of primary importance, and the transformation of the energy of mechanical deformation to other forms of energy, mainly heat, gains importance thereby.

Martens' Crushing Tester

In the year 1908, A. Schob noticed that cracks formed in the axis of a cylinder of an inferior grade of rubber eraser, which he had rolled back and forth under pressure, between two plates. The apparatus of A. Martens, designed and tested on the basis of this observation, to test cylindrically-shaped samples of rubber compound for "crushability," came to nought because it was impossible to keep the sample in the desired path.[57] Martens solved the problem by building a simple reliable crushing apparatus in which a spherical sample (30 mm. diameter), instead of a cylindrical one, rolled in a V-shaped groove under loading.

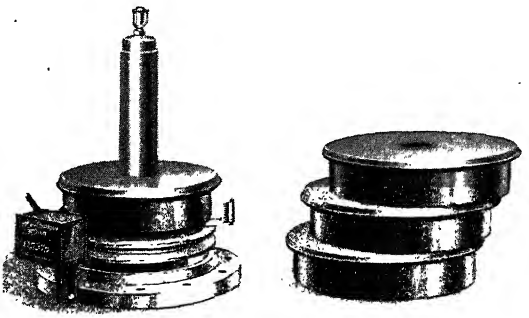


Figure 178—
The crushing tester of
A. Martens.

Figure 178 shows a view of Martens' "crush" tester. The load is transmitted directly to the sample through the pulley (designed for a round belt). By suitable combinations of the weight of the pulley (including the guide pin) with 4 additional weights, the loading of the ball may be varied as desired between 12.5 and 100 kg. in steps of 12.5 kg. For loadings of 37.5, 62.5 and 87.5 kg., a thin shell (not shown in the picture), which is of the same height as the smaller weight, and which together with the pulley makes up a load of 12.5 kg. is used instead of the smaller weight.

[57] See Memmler and Schob. *Mitt. Materialprüfungsamt, Berlin-Dahlem,* **30,** 140 (1912).

A counting device which counts the number of rotations of the pulley (not the ball), is operated by means of a catch placed on the pulley. This count of rotations until the ball is crushed, forms, in connection with the existing degree of loading, the measure of resistance to crushing. With the cylindrical sample (which had to be rejected for the reasons given above) the beginning of crushing could be observed on the end of the sample; however, with a spherical sample such a possibility is lacking, since the destruction begins on the inside near the center of the ball. Differences between soft rubber compounds with respect to the number of revolutions (absolute or relative) which a ball can endure undoubtedly also exist. The end of the test is reached when the belt does not rotate the pulley any more, as a consequence of the bursting of the ball or of the development of a large hollow (due to crushing), which leads to the extreme flattening of the ball.

The mechanical energy which the ball absorbs in rotating under great deformation, is so great that the ball is intensely heated inside. With stiff compounds, the temperature rises beyond the curing temperature. Under otherwise similar conditions, the heating and the number of counts until crushing depend greatly on the speed of rotation, which is, therefore, kept as exactly as possible at a normal speed of 85 r. p. m. (a purely conventional value). The crushing test is generally used for solid tire and tread compounds. It does not work well with very soft or very hard compounds. One soft compound, the investigation of which was prompted by scientific interest only, showed a very noticeable internal heating. The undercured ball (a pure rubber-sulfur mix) was squeezed so flat at the beginning of the test that the greater portion of it was squeezed out of the groove. After several hundred revolutions of the apparatus the sample was cured considerably on the inside because of the heat, thereby becoming stronger, and had pulled itself back into the groove again as a consequence of the building up of an excessive contraction pressure.

No measurement of the energy expended in such a crushing test has been reported up to the present time. For this purpose a determination of the current consumption of the driving motors was made in a few cases at the Materialprüfungsamt. Such measurements would be sufficient for the purpose if it were certain that the friction losses in the driving devices between the motor and the testing apparatus were constant. Because of the magnitude of the friction portion compared to the total work, slight variations in the former affect the measurements to an inadmissible degree.

In the future it may prove to be desirable to measure regularly the energy taken up by the ball.

A. Schob suggested a change in the Martens "crush" tester, which to date has not been made. He proposed that the moment of rotation, resulting from the motive power of the ball, be measured by separating the running groove from the base plate and setting it on a ball bearing. The torque could be determined by means of a spring balance which would prevent the grooved track from rotating.

The ball should be loaded so that it will be crushed in not less than 5,000 nor more than 20,000 rotations of the apparatus. With a greater number of rotations, the unavoidable abrasion of the surface of the ball becomes objectionable, and if such a high compression loading is chosen that only a very low number of rotations are obtained, the material is excessively stressed. If the same relation between the size of the loading of the ball and the number

of rotations required for crushing, existed for all compounds, the fact could have little significance. That such is not the case, however, is readily shown by Figure 179. The data used were obtained with compounds which were customary for solid tires over 15 years ago. The modern solid tires require a higher number of rotations. For the early compounds, as shown in Figure 179, the proper degree of loading was 50 kg.; now 62.5 kg. no longer suffices, and 75 kg. must be used. For shortened notation it is recommended that the number of rotations of the apparatus required for the crushing of the ball, be designated as "crushing number," and that the value for the loading be given after the "crushing number," separated by a line; as for instance, 12,300/62.5.

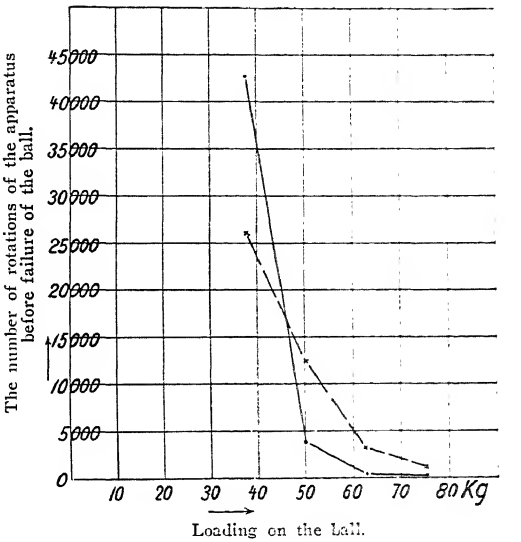


Figure 179—The relation between "crushing number" and the loading on the ball, with two different solid tire stocks. (Carried out in 1914. Modern compounds give much higher values.)

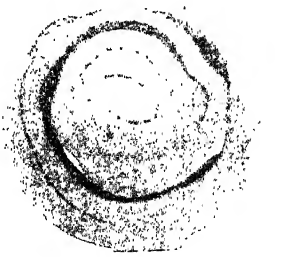


Figure 180—Appearance of a ball, vulcanized in a spherical shape, at the conclusion of the crushing test.

Because of accidental circumstances, the method of preparation of the test ball has not been made public by the Materialprüfungsamt, and so it happens that, in spite of the fact that the crushing test was introduced years ago, there still exists some confusion in regard to the preparation of the ball. A thorough description of the preparation of the balls, as carried out in the Materialprüfungsamt according to the method of A. Schob, is therefore in order.

The idea of curing the sample in ball form is to be rejected. The manner

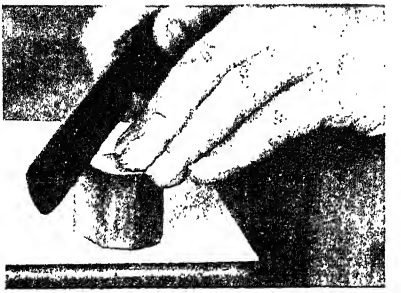


Figure 181—Method of preparation, starting with the cube which was cut out of a block with a knife.

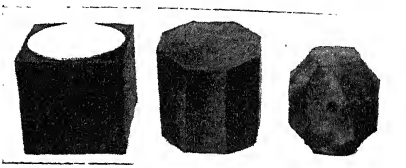


Figure 182—The different steps in the preparation, using a knife.

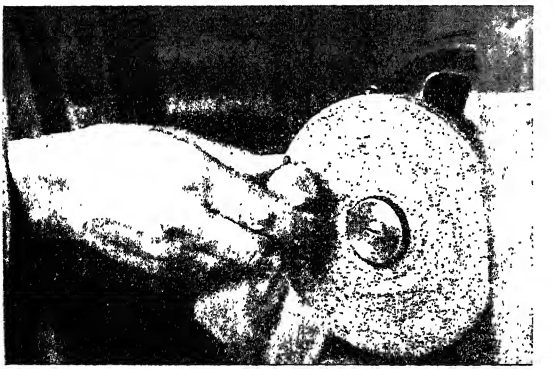


Figure 183—Grinding the sample to a spherical shape, using the side of the emery wheel.

Figure 184—The different steps in grinding.

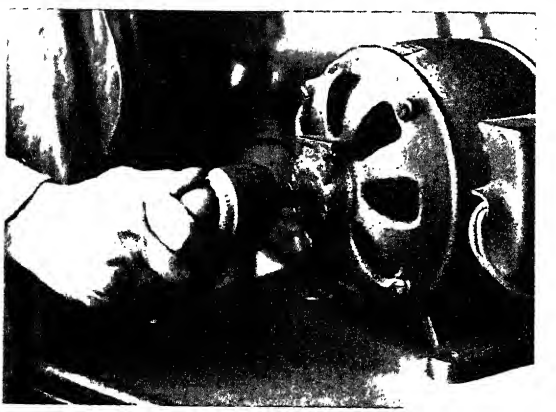


Figure 185—Smoothing the surface of the ball on a properly shaped emery wheel.

Figures 181 to 185—The preparation of balls for the crushing test.

of destruction of the sample during the test (*see* Fig. 180) clearly shows the insufficiency of such a method of preparation. To this is added the fact that a crushing test alone is not sufficient for judging a rubber mixture; tension tests should also be run. The compound is therefore cured in blocks, 190x70x40 mm., in a heater, with a 30 minute rise to 292° F. and a constant temperature of 292° thereafter. Out of such a block, 10 large normal rings in an emergency also the same number of small ones; (*see* p. 540) and 4 balls (30 mm. in diameter) can be produced. This set of samples is usually also sufficient for a series of aging tests. The block is first cut by hand with a knife wetted with soapy water. (See the procedure given in the series of illustrations shown in Figs. 181 to 185.) Cube-shaped blocks, with edges approximately 35 mm. in length, are formed. A round lead disc, 32 mm. in diameter, is then placed upon the upper surface of the cube with the left hand, and by guiding from it, cuts are made on all four edges with the knife. An eight-edged prism thus resulting (Figs. 181, 182a, b). The edges on the ends of the prism are then cut off by hand (Fig. 182c). The sample is next ground on the lateral face of an emery wheel (approximately 150 mm. in diameter) which is fastened to the shaft of a 1/6 H. P. motor which runs at 1500 r. p. m. (Fig. 183). The resulting rubber dust is sucked off at the side by a ventilator. Upon this wheel the ball is ground down by hand to a 30 mm. diameter, with a deviation of not more than $\pm$ 0.1 mm. The last grinding upon the forming wheel (Fig. 185) takes off only a very small amount of material and is only done to smooth the surface.

The grinding of the sample on the even lateral surface of the 150 mm. emery wheel is conducted according to the following steps (Fig. 184):

(1) Cylinder to a diameter of 30 mm.
(2) Cylinder height to a measured 30 mm.
(3) The third operation may be carried out in two ways, according to the inclination of the grinder; either
(a) In the manner of operation (2) by grinding cylinders around the two other axes, and leaving the wedges (visible in the second sample of Fig. 184) to be ground off last, or
(b) By grinding the one-half immediately down to the half sphere (Fig. 184, third sample) and then following it with the other half.

After the ball is ground with an exactness of $\pm$ 0.1 mm. by either one of these methods it is smoothed on a hollow grindstone, as is shown in Figure 185. The resulting ball is shown in Figure 184 (fourth sample).

The skill in grinding balls is not hard to acquire. According to whether the compound is easy or hard to grind, a skilled grinder requires 15 to 20 minutes to prepare a ball, including the time for cutting with the knife.

FLEXOMETERS

F. D. Abbott [*Ind. Eng. Chem.*, **20**, 853 (1928)] has described experiments involving a test similar to the crushing test in its arrangement and in the destructive effect of the test on the sample.[58] The breakdown observed in the rubber cushions upon which automobile springs have recently been fastened, led to the attempt to imitate the stressings of such a cushion in some mechani-

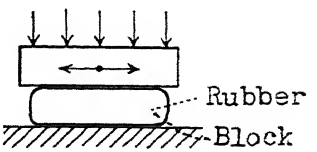
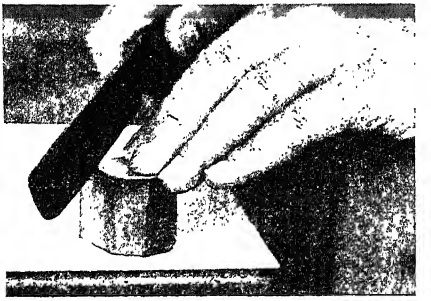


Figure 186—The principle of F. D. Abbott's method of testing.

[58] Translator's Note. "Blow out" test is the name applied to this test.—V. N. M.



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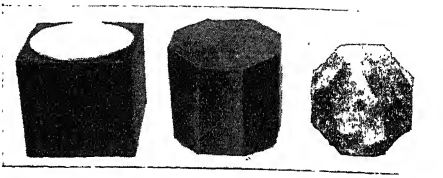

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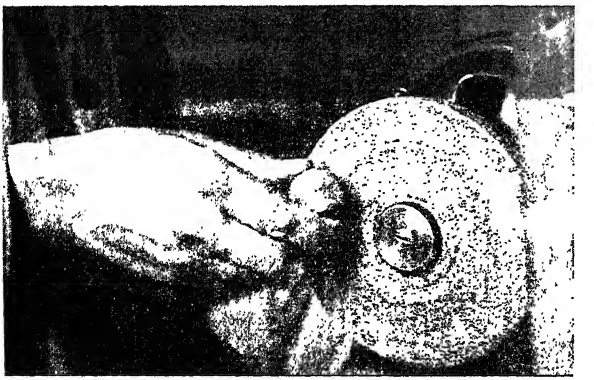
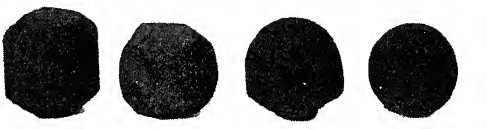
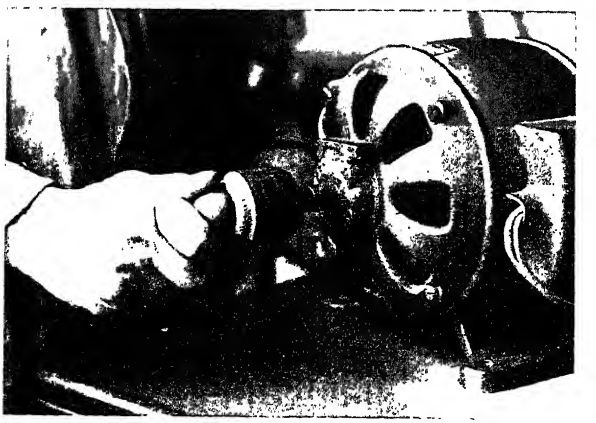


Figure 183—Grinding the sample to a spherical shape, using the side of the emery wheel.

Figure 184—The different steps in grinding.





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Figures 181 to 185—The preparation of balls for the crushing test.

of destruction of the sample during the test (*see* Fig. 180) clearly shows the insufficiency of such a method of preparation. To this is added the fact that a crushing test alone is not sufficient for judging a rubber mixture; tension tests should also be run. The compound is therefore cured in blocks, 190x70x40 mm., in a heater, with a 30 minute rise to 292° F. and a constant temperature of 292° thereafter. Out of such a block, 10 large normal rings (in an emergency also the same number of small ones; (*see* p. 540) and 4 balls (30 mm. in diameter) can be produced. This set of samples is usually also sufficient for a series of aging tests. The block is first cut by hand with a knife wetted with soapy water. (See the procedure given in the series of illustrations shown in Figs. 181 to 185.) Cube-shaped blocks, with edges approximately 35 mm. in length, are formed. A round lead disc, 32 mm. in diameter, is then placed upon the upper surface of the cube with the left hand, and by guiding from it, cuts are made on all four edges with the knife, an eight-edged prism thus resulting (Figs. 181, 182a, b). The edges on the ends of the prism are then cut off by hand (Fig. 182c). The sample is next ground on the lateral face of an emery wheel (approximately 150 mm. in diameter) which is fastened to the shaft of a 1/6 H. P. motor which runs at 1500 r. p. m. (Fig. 183). The resulting rubber dust is sucked off at the side by a ventilator. Upon this wheel the ball is ground down by hand to a 30 mm. diameter, with a deviation of not more than $\pm$ 0.1 mm. The last grinding upon the forming wheel (Fig. 185) takes off only a very small amount of material and is only done to smooth the surface.

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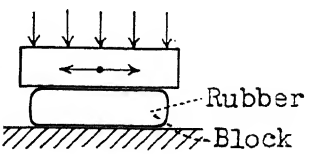


Figure 186—The principle of F. D. Abbott's method of testing.

[58] Translator's Note. "Blow out" test is the name applied to this test.—V. N. M.

cal test. The scheme of the mechanical arrangement is seen in Figure 186. The rubber sample is squeezed between two level iron plates, either under constant load or constant compression. The upper plate moves back and forth, while the base plate is held motionless. The maximum stroke of Abbott's machine is 10 cm. In the experiments up to the present a stroke of about 1 cm. has been used, with a frequency of 800 strokes per minute. The samples show a compression set ("static set under compression") very quickly. With longer testing, the appearances of destruction similar to those of the crushing test, are obtained; i.e., intense internal heating, destruction inside with evolution of gas, and finally the bursting of the sample. Abbott has also carried out experiments with oscillating torsion stressing, and has compared the results of the new kind of test with the results of the customary test. Whereas, as is expected and as is found in the case of the crushing test, the results of individual tests (hardness, compression set after a static compression stress, tear tests) show no regular correlation with the new test, it gives a relatively good agreement with the hysteresis loss. The original work must be referred to for the data in detail.

The latest development* in connection with laboratory machines for testing the resistance to fatigue of rubber compounds is the flexometer designed by R. W. Allen and described by L. V. Cooper. [*Ind. Eng. Chem., Anal. Ed.*, **5**, 350 (1933)] (*See* Figure 186a). The operation of the machine consists simply of compressing, under definite load, a block of rubber between two plates, one of which is stationary, and the other of which travels in a circular motion of definite magnitude at a rate of oscillation of 800 per minute. Both the loading and magnitude of the circular motion may be varied widely.

Laboratory test blocks are cured in the shape of a frustum of a rectangular pyramid, the object of using this shape being to insure that samples can be removed from the molds without difficulty, regardless of the nature of the stock. Test blocks of cured articles may be cut into any desired size and shape, provided their height is not more than 2 inches (5.08 cm.) which is the maximum distance between plates.

Each of the plates has a center inset of wood, 3 inches (7.62 cm.) in diameter and 0.5 inch (1.27 cm.) thick. The rubber test block is placed between the wooden blocks, which act as heat insulators and tend to hold the generated heat in the rubber.

The machine is provided with electrical bell-ringing contacts which are adjusted a definite distance apart. As the test block is deflected under the testing conditions, the upper contact is carried downward toward the lower contact, since the load, which is a dead weight, continues to rest on the yielding block. The bell does not ring until the block has been deformed enough to allow the contacts to close. The duration of the test, which is measured from the time the circular motion starts until the bell rings, can be altered by changing the position of the contact points. If the test is continued sufficiently long, the block will actually "blow out," or shatter to pieces. In the case of the flexometer described by Cooper, the oscillation is stopped before blow-out, as it has been found that the downward movement of the load during operation of the machine provides a definite criterion of the condition of the center of the test block. Tests have shown that all blocks of similar composition yield the same distance at the time porosity begins to develop within them.

Temperature rise or heat generation measurements may be made with this flexometer by inserting thermocouples and recording the temperature after a certain amount of work has been done on the block.

The reader is referred to the original article for details in connection with operation of the flexometer.

Abrasion Tests

Testing methods which are expected to determine the resistance of a material to mechanical abrasion or grinding, must overcome numerous difficulties in all lines of material testing. The greatest of these is the problem of obtaining a grinding material which works uniformly, since the material itself is attacked during the test. The proper selection of the granulation of

* Translator's note by V. N. M.

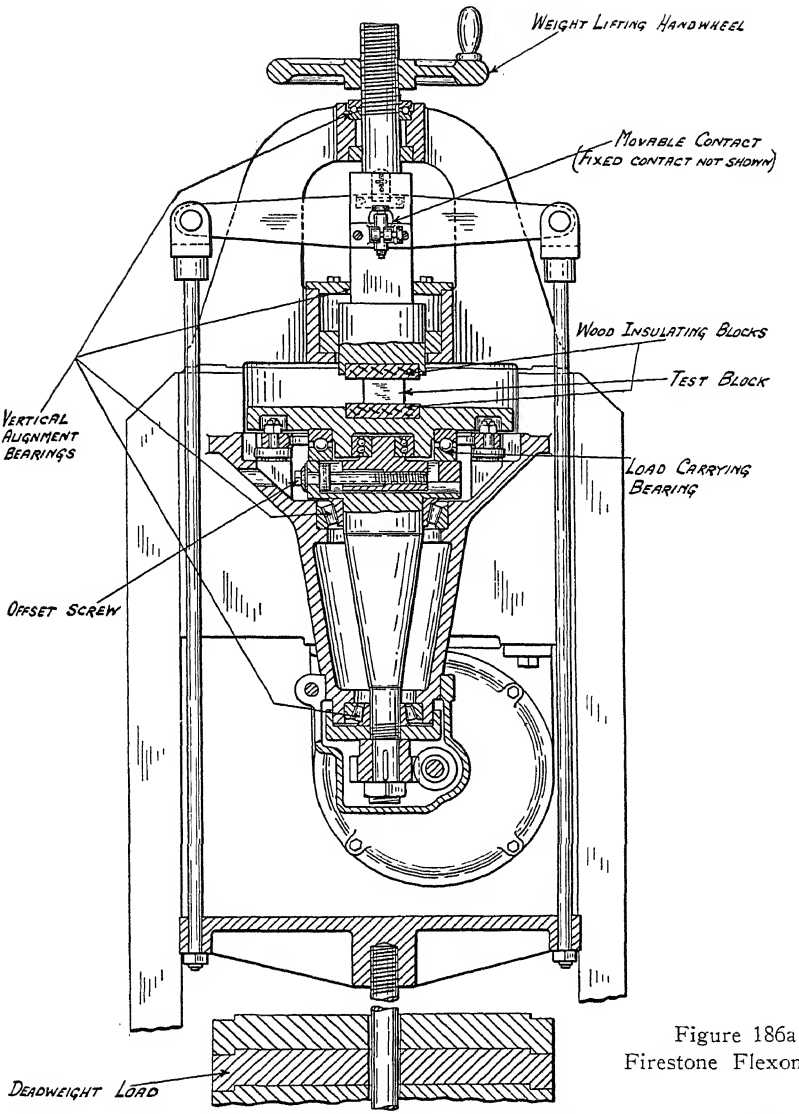


Figure 186a
Firestone Flexometer

the grinding material, the pressure, the kind of movement, and finally the speed, constitute further sources of difficulty.

A test based on the old experiments of A. Martens [59] with linoleum, was first carried out, using the method described below.[60] The sample is ground off on a grindstone, to the surface of which a constant supply of sand is applied. The loss of weight of the sample after a definite period of grinding determines the extent of the abrasion. The sand added during the course of the test was supposed to maintain a uniform gripping surface on the grind-

[59] Martens, A., "Über Abnutzung durch Schleifen," *Mitt. Materialprüfungsamt, Berlin-Dahlem*, **4**, 3 (1886).

[60] See Memmler and Schob, *Mitt. Materialprüfungsamt, Berlin-Dahlem*, **30**, 145 (1912).

stone. In spite of all possible care, it has been found to be impossible to transfer this method to soft rubber testing, and to so modify it that useful results may be obtained.

A sand blast,[61] which is useful for testing the abrasion resistance of flooring materials (natural paving stones, artificial stones and floorings of all kinds, terrazzo, wood, linoleum, etc.), was tried next. With this method also the elastic properties of the rubber prevented the production of sufficient abrasion in a one-hour test (a 3-minute test is sufficient with the building materials mentioned above).

Horizontal porcelain drums, which are filled with nut-size field stones and rotated on rolls for the purpose of disintegrating building materials, were also tried for the abrasion testing of soft rubber. Fifty cubes, 6 mm. on an edge (equal to the slab thickness of the rubber slabs to be compared) were placed in each drum, with approximately 3 kg. of field stones and 1 kg. of standard sand as the abrasive material. The loss in weight of the rubber cubes after a definite length of rotation was to serve as a measure of the abrasion. Even after a 60-hour test, the loss in weight was so small and the difference between the tested materials was so slight that no practical method for testing the resistance of rubber to abrasion could be developed.

These futile tests finally induced a former mechanic in the Materialprüfungsamt, W. Mai, to try the method of allowing the rubber sample to rotate in a loose grinding material. This method then led to useful results.

The testing arrangement, which has the advantage of great simplicity, is shown in Figure 187. A glass vessel, approximately 80 mm. in diameter and

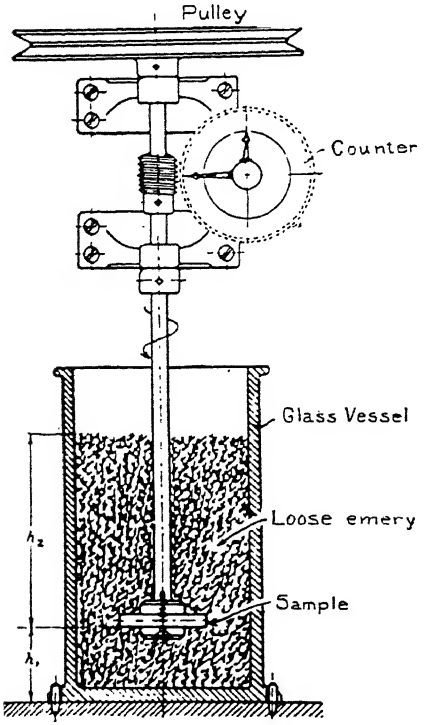


Figure 187—The abrasion test of W. Mai.

[61] See Gary, M., "Versuche mit dem Sandstrahlgebläse," *Mitt. Materialprüfungsamt, Berlin-Dahlem*, **19**, 211 (1901).

190 mm. in height, is almost filled with a loose emery of definite particle size. The rubber sample, in the form of a disk, is fastened to the lower end of a hardened steel shaft, which is driven by means of a pulley and which is imbedded in the emery. The loss in weight of the sample after a definite number of revolutions serves as a measure of the abrasion.

The test results were expected to be influenced by variation in the particle sizes of the emery used, different heights of the emery layer over and under the sample, different widths of the vessel, condition of the walls of the vessel itself, different rates of rotation, and the abrading capacity of the emery itself. A clearer understanding of the magnitude of these influences was obtained in a series of tests.

Table 18 gives the individual results of such tests with a definite emery particle size, with varying heights of the emery layer above and below the sample, as well as with various speeds of rotation.

TABLE 18.—*Abrasion Experiments in Coarse-grained Loose Emery.*

(Each experiment running for 10,000 revolutions.)

Material	Height of the emery layer: Under the sample h_1 cm.	Height of the emery layer: Over the sample h_2 cm.	Rev. per min. n	Results of the Experiment: The loss in weight of the sample after 10,000 revolutions: $\Delta g\%$ — Individual values 1	2	3	4	5	Average values	Remarks
Xa	3	10	125	2.7	2.6	2.5	2.8	2.7	2.7	The influence of the height h_1
Xa	5	10	125	2.6	2.6	2.8	2.5	2.6	2.6	
Xa	7	10	125	2.9	2.6	....	....	....	2.7	
Xa	3	5	125	0.6	0.6	0.7	0.8	0.6	0.7	The influence of the height h_2
Xa	3	10	125	2.7	2.6	2.5	2.8	2.7	2.7	
Xa	3	15	125	6.3	5.7	6.1	6.6	5.9	6.1	
VIIc	3	5	125	6.0	6.4	5.9	5.8	5.6	5.9	
VIIc	3	10	125	18.2	18.2	18.5	18.7	18.6	18.4	
VIIc	3	15	125	30.7	31.1	29.9	30.2	29.7	30.3	
Xa	3	15	70	4.3	4.5	4.8	5.1	4.7	4.7	The influence of the number of revolutions per min. n
Xa	3	15	125	6.3	5.7	6.1	6.6	5.9	6.1	
Xa	3	15	220	4.5	4.3	4.9	4.3	5.1	4.6	
VIIc	3	15	70	28.5	26.7	28.8	29.5	28.8	28.5	
VIIc	3	15	125	30.7	31.1	29.9	30.2	29.7	30.3	
VIIc	3	15	220	29.0	29.1	30.2	31.0	33.1	30.5	

From this table it may be concluded

1. The height of the emery layer (h_1) under the sample has no influence on the degree of grinding loss, within the limits chosen. It is suitable to work with at least 3 cm. of emery under the sample.

2. The grinding loss increases with the increase in height of the emery layer (h_2) above the sample. For comparative tests a constant height (h_2) of 15 cm. is satisfactory.

3. Within the limits tested, the speed of rotation has no significance. The disagreement in the values in the series for the material Xa, with $n = 125$, is due perhaps to the fact that the tests with $n = 125$ were carried out directly after the arrival of the material from the factory, while those with $n = 70$ and 220 were not carried out until several weeks after the arrival of the material. The Material VIIc was already older, so that the time difference of several weeks made no difference with this material, while with material Xa it evidently caused the varying values.

It was thought that the layers of emery which had nothing to do with the actual grinding of the sample, could be replaced by an equal weight of other material (which could be placed on a thin layer of emery and could thus reduce the quantity of emery required). However, experiments showed that other results were then obtained. Nevertheless, it is not necessary to renew the total amount of the emery every time a replacement is made. The upper layer, down to that which has actually come in contact with the sample, may be removed for subsequent use, provided care is used in the removal.

In regard to the usefulness of the method, the question of the number of tests for which a single batch of emery is serviceable, without influencing the degree of grinding loss of a rubber sample, is of considerable interest. In order to answer this question, experiments (sometimes lasting through 100,000 revolutions) with several kinds of rubber compounds were carried out without renewing the emery. After a definite number of revolutions (5,000 revolutions as a rule) the loss in weight of the sample was determined. As a consequence of the stirring effect resulting from the removal and replacement of the sample, the most "worn out" emery in the vicinity of the sample, is distributed evenly throughout the whole mass of emery.

According to the results in Table 19, it appears that the degree of loss on grinding diminishes with every additional 5,000 revolutions after the first 10,000. This can be due partially to the fact that the exposed surface of the rubber sample is diminishing, because of the loss on grinding. Therefore, each sample should be run in the apparatus for only 10,000 revolutions (without weighing at 5,000 revolutions). The sample should then be removed, the weight of the sample determined, and the emery renewed for the next test.

TABLE 19.—*The Influence of the Length of the Test Upon the Abrasive Action of the Emery.*

Number of Revolutions	Loss in weight of the sample after each 5,000 revolutions Δg in per cent		
	Material X	Material Vb	Material II
5,000	2.3	2.6	7.1
10,000	2.3	4.1	8.2
15,000	2.0	3.2	7.2
20,000	1.8	2.5	5.3
25,000	1.8	2.2	3.5
30,000	1.7	1.9	2.7
35,000	1.5	1.9	....
40,000	1.4	2.1	....
45,000	1.4	1.8	....
50,000	1.4	1.4	....

It is best not to take the initial weight of the sample until after it has been ground for approximately 500 revolutions in order to roughen the surface. Spent emery is used for this preliminary grinding.

In order to obtain reproducible results, an emery of the same particle size should always be used, for naturally in changing to other sizes different grinding losses are obtained. The particle size chosen for the experiments described above, No. 5½ Naxos Union, has proved to be very suitable.

The condition of the inner wall of the vessel has an important influence upon the test results. Iron vessels give values essentially different from those of glass vessels. In a new glass vessel, a sufficiently constant roughness is obtained only after 5 or 6 tests, so that after renewal of the vessel the results of the first 5 or 6 tests should be rejected.

The usual sample is the waste disk of the large normal rings (*see* p. 540) used for tension tests. These disks are 6 mm. thick and 44.6 mm. in diameter, and are perforated in the center so that they may be used in the Mai Apparatus. Comparative results cannot be obtained from samples varying in size. In some cases, small pieces carefully glued together may be used.

The grinding apparatus used by the B. F. Goodrich Company [62] is based on the same principle as the apparatus built by Mai in 1912. The main differences arise from the multiple arrangement of the samples in a vessel, the attachment of several vessels to a common power source, and the use of iron vessels.

The advantage of the use of the grinding material in a loose granulated form is the reproducibility of the test conditions from the standpoint of the gripping properties or the "grinding force." The disadvantage is that the grinding force cannot be expressed numerically.

The disadvantage just mentioned explains why certain investigators have turned back again to the principle of the grindstone. In the newer apparatus, a constant grinding power is maintained for each test by renewing the covering of emery paper or emery cloth, which is glued to a wood or metal wheel.

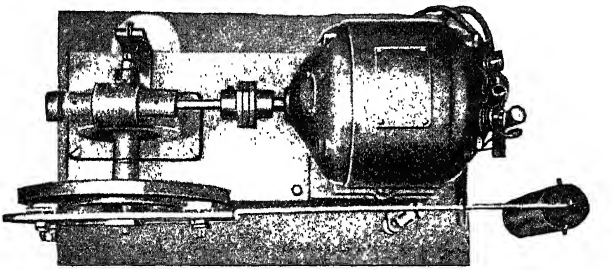


Figure 188—The Grasselli Abrasion apparatus (as viewed from above).

The apparatus of the Grasselli Chemical Co., shown in Fig. 188,[63] is one of this type. The grinding disk is mounted on a hollow shaft which is driven by an electric motor by means of a worm gear drive. The lever which carries the two test blocks (mounted diametrically opposite each other) is attached to an axis which extends through the hollow shaft. A weight which is attached to the shaft and which acts over a pulley presses the samples against the grinding disk. A spring balance and a variable weight are attached to the lever which holds the samples, so that the turning moment caused by the grinding resistance between the sample and the grinding surface may be measured, thus making it possible to determine the work of grinding. The more recent apparatus is furnished with a blowing or suction device for the removal of the rubber dust, so that the grinding properties of the emery surface can be kept more uniform during a test.

A somewhat different principle, which is (in the opinion of the writer) decidedly worthy of note, is that utilized in the apparatus of the Akron Standard Mold Co., shown in Fig. 189.[64] The sample (a round disk) mounted on a shaft, is driven by an electric motor by means of a worm gear. The abrasive wheel (Carborundum) is so easily rotated that it is set into motion when it comes in contact with the revolving sample. It is pressed

[62] See *India Rubber World*, **70**, 506 (1924).
[63] Handbook of the R. T. Vanderbilt Co., New York, p. 74, **1927.**
[64] Handbook of the R. T. Vanderbilt Co., New York, p. 73, **1927.**

against the sample by a weight which is placed on the weighing scale (shown at the right) which acts on the abrasive wheel by means of a system of levers. The axis of rotation of the sample can be set at any angle up to 40° to the axis of rotation of the abrasive wheel. The slippage taking place when the axes are set parallel to each other is only that resulting from the pressure between the sample and the abrasive wheel. When the axes are set at an angle, an additional slippage occurs. This test method approaches more closely the conditions prevailing during actual road testing.

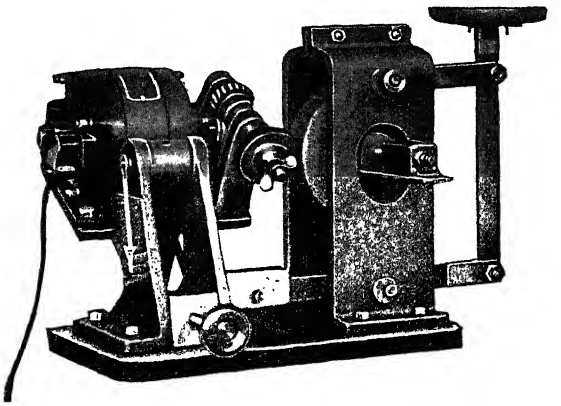


Figure 189—The abrasion apparatus of the Akron Standard Mold Company.

Another abrasion tester of the angle-slip or constant-slip type is the one of simple design used by the B. F. Goodrich Co.* [Tronson, J. L., and Carpenter, A. W., "Abrasion Tests of Vulcanized Rubber Compounds Using an Angle Abrasion Machine," *Proc. Am. Soc. Testing Materials,* **31,** Part II, 908-922 (1931)]. The sample disk is placed on the shaft of one motor while the abrasive disk is placed on the shaft of another. The abrasion test may be conducted with either motor providing the power. The results with this instrument parallel those obtained in service fairly well.

A comparison of four types of abrasion machines used today has been made by C. A. Klaman. [*Proc. Am. Soc. Testing Materials,* **31,** Part II, 936-941 (1931).] He found that all these machines gave results which agreed with road service satisfactorily in the case of stocks cured to the optimum, but did not give good correlation with over- or under-cured stocks.

It is evident from the discussion on abrasion testing [*Ibid.,* **31,** Part II, 942-954 (1931)] at the Symposium on Rubber of the American Society for Testing Materials in 1931, that as yet no satisfactory apparatus has been designed which actually duplicates service for all types of stocks and all degrees of vulcanization. The various factors which influence the laboratory results were considered from the point of view of the possible causes of the discrepancies between these results and those obtained in actual service. Some worth-while developments should result from this discussion.

The reader is also referred to the article by L. J. Lambourn [*Trans. Inst. Rubber Ind.,* **4,** 210 (1928)] in which is discussed the controllable "slip" machine of the Dunlop Rubber Company, the reasons for the development of a machine of this type, and various results obtained by its use.

Determination of Resistance to Tear ("Kerbzähigkeit")

General Conception

Many materials, especially those which are called brittle, are very sensitive with respect to surface injuries when they are under tension; that is, the tension which caused rupture is smaller when nicks or notches are present,

* Translator's note by E. O. E.

than when the surface is smooth. This tendency of the materials to tear when notched or cut is especially noticeable when the tension is applied either in a jerky manner, or smoothly but as repeated (oscillating) stresses. If a material has a low sensitivity toward sudden cross-sectional changes (notches) when under stress, it is designated in German as "kerbzäh."

It has not yet been possible to establish any regular relationships between this property and the other properties of materials (tensile strength, deformation capacity, elasticity, etc.). Experiments which determine directly the capacity for resisting the effect of notching or cutting are therefore required. Unfortunately, the carrying out of such test procedures is generally very difficult. The test results, which cannot as yet be expressed in terms of any numerical measure, depend on the material itself as well as on the form and size of the notch or cut, and on the size of the notched cross section in relation to a similar unnotched cross section.

Although soft rubber is not generally classified as brittle, it is nevertheless "notch sensitive," the sensitivity varying according to the degree of vulcanization and the kind of compound. Overcuring increases this sensitivity.

By subjective testing (scratching on the edges with the finger nail, or tearing a sheet which was previously cut on the edge) the "Kerbzähigkeit" (resistance to tear) of soft rubber compounds can be determined fairly well. The development of objective methods meets with very great difficulties, especially in regard to the reproducibility of the initial notch or cut, which should be very exact with soft rubber. The knife, with which the initial cut is made, must be as sharp as a razor. The radius of curvature of such a cutting edge is not sufficiently exact to be measured. A change of several hundred per cent occurs in the radius of curvature after very short use of the edge (a fact which has been known for a long time in the case of razors). To this is added the fact that the initial cut is very seldom located in the plane of cleavage of the material; that is, the usually irregular plane of lowest resistance to tear, produced principally by the fabrication process. Because of this, a relatively large force is required at the beginning of the tearing. The forces afterwards needed to continue the tearing is measurable with but little accuracy, because the tearing proceeds in jerks (influence of speed) and the plane of cleavage runs irregularly.

Since, as previously mentioned, only very limited conclusions (often none at all) regarding resistance to tear can be drawn from other types of physical tests, and since investigators in neutral scientific laboratories prefer not to use such sensitive subjective (hand) tests as those mentioned above, earnest efforts must be made to use objective tests, even though they cannot be carried out within the limits of accuracy allowed for other kinds of tests. One must always remain aware of this degree of inaccuracy. Tearing toughness has, however, a very great importance in the practical usage of soft rubber, and that is why a few objective tests for the determination of tearing toughness are briefly discussed below.

Various Test Methods

E. C. Zimmerman [65] uses thin strips of rubber, 3 in. x 9 in. x 0.1 in. for the determination of resistance to tear. The strips are prepared with a 1/2" cut in the center (*see* Fig. 190) and are torn apart between the hooks of a

[65] Handbook of the R. T. Vanderbilt Co., p. 79, New York, 1927; also, *Rubber Age (New York)*, **12**, 130 (1922).

tensile-testing machine. A convenient rate of separation of the hooks is from 2 inches to 6 inches per minute. For comparative tests, a definite speed must naturally be maintained. From the autographic chart obtained during the running of the test, the work W required to tear the sample may be calculated by using the following formula:

in which
K = the number of inch pounds represented by a square inch of area on the chart,
A = the area in square inches under the curve, representing work,
F = the final value of the force necessary for the tearing,
E = the elongation of the sample in inches (distance between the hooks, minus L),
L = the length of the tear produced by the machine, and
t = the thickness of the sample strip.

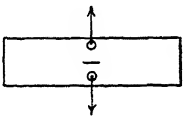


Figure 190—The sample for determining resistance to tear used by E. C. Zimmerman.

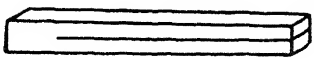


Figure 191—The tearing test sample used by W. Heidensohn.

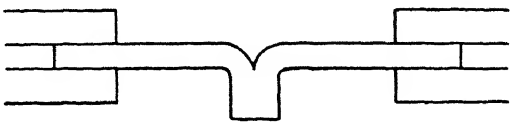


Figure 192—The tearing test used by W. Heidensohn.

W. Heidensohn has recently carried out tearing tests on various carbon black mixtures in the Materialprüfungsamt. From the waste disks from the normal rings (*see* p. 540) he cut out strips, which were square in cross section (6x6 mm.), and as long as the diameters of the disks. These strips were cut lengthwise through the center with a razor, leaving 10 cm. on the ends uncut. (*See* Fig. 191.) The ends were fastened in a tensile-testing machine, as shown in Figure 192. The square cross section was chosen so that the tearing test could be carried out with the initial cut made either as shown in Figure 191 or in the direction perpendicular to that shown, without requiring any allowance to be made for change in the influence of the cross section.

The advantages of this method lie in the simple procedure required for preparing and testing the samples, and in the identity of the test materials with those used for the tensile, elasticity and abrasion tests (also with the crushing test, if the samples are made out of blocks). One disadvantage, arising from the short distance which is available for tearing, is that the only tear resistance which can be measured is the one which occurs at the beginning of the tearing. This initial resistance is doubtless higher than the actual tear resistance of the material. Nevertheless, Heidensohn found a considerable difference in the tear resistances of a great number of compounds, which

exhibited no such distinct differences when tested by any of the other methods (tension, crushing and elasticity tests). The clear differentiations possible between compounds (agreeing with the subjective [hand] test evaluations which have been used for years), and the agreement of results obtainable in the case of several parallel experiments, make this method of tear testing appear useful.

A few figures from tests on solid tire compounds containing carbon black may illustrate this. (*See* Table 20.)

TABLE 20.—*Several Experiments on Tear Resistance (by Heidensohn).*

Material No.	Tension test σ_z kg./sq. cm.	Tension test δ_z per cent	Permanent set (stretching test) δ' per cent 5 min. After release of tension	Permanent set (stretching test) δ' per cent 24 hr. After release of tension	Impact test η_{el} per cent	Crushing number (See p. 591)	Abrasion test (Mai's method) ΔG per cent	Resistance to tear kg./cm.
1	213	545	15.2	9.7	48	1,900/62.5	1.0	16
6	171	396	10.2	7.8	55	10,200/62.5	1.2	12
9	144	336	7.6	5.5	57	7,500/62.5	2.0	14
17	227	520	13.0	9.8	49	8,200/62.5	1.4	20
19	237	500	11.2	7.8	50	17,700/62.5	....	22
24	110	209	.....	....	39	12,000/62.5	....	2
25	85	260	.....	....	49	20,000/62.5	....	8
27	81	306	6.4	4.3	31	1,100/62.5	....	4
28	107	383	7.2	5.2	39	2,100/62.5	....	3

Of all the materials tested (all of them are not given here), No. 19 had the greatest and No. 24 had the least resistance to tear. No. 24 had the lowest value for the ratio between tear resistance and tensile strength while No. 9 had the highest value.

D. D. Wright [66] tried to determine the tensile strength and the tear resistance with a single sample, by means of a peculiar method. He puts two slits, 2/3 of the length, in the tensile sample (a strip 127 mm. long and 36 mm. wide). The upper uncut end is placed with the entire width in the upper clamp of a tensile machine, while the tongue-shaped center portion of the lower end of the sample is placed in the bottom clamp. When the sample is thus stretched, the loose ends of the sample turn out at an angle. The writer doubts that sufficiently clear results can be obtained by this method.

A modification of Wright's method has come into practice in several laboratories.* This consists of putting the tongue-shaped portion in one clamp and the two loose margins in the other clamp and pulling until a complete separation occurs. This method is definitely a tear test and not a modified tensile test.

A tear test variously known as the Winklemann tear test, the crescent tear test, and popularly as the peanut test has been used for a number of years by the B. F. Goodrich Company. [See Carpenter, A. W., and Sargisson, Z. E., "Study of a Test for Tear Resistance of Vulcanized Rubber Compounds," *Proc. Am. Soc. Testing Materials,* **31**, Part II, 897-907 (1931).] The method consists in subjecting a crescent-shaped test sample to such a tension as to produce tearing. Five slits are made in the inner curved surface of each specimen. The load required to separate the specimen is used in calculating the resistance to tear. The actual tearing is always along the grain under the conditions of the test. Thus the tearing force is that which is required to separate the fibrous structures of the rubber rather than that necessary to break the fibers themselves. The resistance to tear of a given compound as measured by this test appears to be related to the tensile strength, the modulus and the resistance to abrasion of the compound.

G. Lefcaditis† and F. H. Cotton [*Trans. Inst. Rubber Ind.,* **8**, 364 (1932)] have recently published a discussion of all previously-developed methods for testing resistance to

[66] *Kautschuk,* **5**, 52 (1929); *Ind. Eng. Chem., Anal. Ed.,* **1**, 17 (1929).

* Translator's note by E. O. E.

† Translator's note by V. N. M.

tear, and have shown a diagrammatic comparison of the various types of test pieces employed in these tests. These investigators have also described their own method, which requires a test piece taken from the inner disc of a 6 mm. Schopper ring. The piece is cut by means of a standard dumb-bell die. The resulting butt-ended test piece is slit along the middle to a distance of 4 mm. from the end. The two wings of the test piece are attached to the clamps of a Scott tester and the remaining 4 mm. is torn. The mean of the initial and the final dial readings is taken as the "tearing load," which is calculated in kg. per cm. thickness of the test piece.

The Aging of Vulcanized Rubber *

Manifestations of and Probable Reasons for Natural Aging—Aging Investigations

All soft rubber goods have only a limited life; they age and gradually deteriorate, becoming hard and brittle. Oxidation of the rubber hydrocarbon has long been recognized as the reason for this phenomenon. Soft rubber, like raw rubber, is chemically highly unsaturated; this makes it possible for oxygen to add at the double bonds not yet saturated with sulfur. The correctness of considering aging as an oxidation process is shown by the fact that vulcanized rubber can be kept almost indefinitely if air and light are excluded. E. Kindscher [67] showed that the formation, found in the middle German brown coal (lignite) deposits and called "Monkey hair" by the miners, contained dried latex particles from the rubber plants [68] which had been involved in the coal formation. This rubber had become more or less vulcanized by the sulfur compounds formed during the decay, i.e., carbonization of the plants, and had so well withstood the extraordinarily long period of aging that the soft rubber-like vulcanizate, after removal of the resin, was still remarkably extensible and elastic.

Granted that the oxygen of the air certainly plays an important part in the aging of soft rubber goods, the situation is nevertheless not so simple as it might appear at first sight. Rubber goods of quite different stability can be obtained from the same rubber mixing, depending upon the conditions of preparation. The vulcanization relationships are, as practical experience has shown, of outstanding significance.

The first systematic investigation along these lines was by Stevens.[69] He used a mixing which consisted of 90 parts of pale crepe and 10 parts of sulfur. Test pieces of this composition were vulcanized for different lengths of time at 134.5° C. and after a definite period of storage in the dark at room temperature were investigated for physical properties. The results are given in Table 21.

According to this work, the tendency to age appears to be, in high degree, dependent upon the size of the coefficient of vulcanization. The product vulcanized for 4½ hours had a vulcanization coefficient of 5.0, and when freshly cured, had the highest tensile strength. During storage, however, this fell off in a very disastrous manner and, after an aging period of 311 days, had become next to nothing. On the other hand, the test piece vulcanized for 3 hours with a coefficient of 3.2, had at the start a considerably lower tensile strength than the sample vulcanized for the longer period of time, but after aging for 311 days it had improved appreciably and surpassed

* Written by E. Kindscher.

[67] *Ber.*, **57**, 1152 (1924).

[68] According to investigations of K. A. Jurasky [*Braunkohle*, **27**, 1130 (1928)] these were a species of *Ficus*.

[69] *J. Soc. Chem. Ind.*, **35**, 872 (1916).

TABLE 21.—*Aging Experiments of Stevens.*

	Aging (days)	Time of Vulcanization (hours) 2	2½	3	3½	4	4½
Breaking strength grams/sq. mm.	4	900	1230	1510	1690	2010	2480
	125	950	1550	1610	1930	1760	1760
	203	1010	1500	1630	1740	1480	490
	311	920	1400	1640	1480	1330	170
Elongation at break	4	1151	1098	1078	1013	987	953
	125	1016	1017	991	952	897	851
	203	1042	1032	1004	936	858	611
	311	1035	1009	993	894	822	372
Tensile product	4	110	136	162	170	199	236
	125	93	153	159	183	158	150
	203	105	155	163	163	127	130
	311	95	141	163	132	109	6
Coefficient of vulcanization	—	2.0	2.6	3.2	4.1	4.5	5.0

in this respect the strength of all the other samples. The same thing was true, though to a lesser extent, of the sample cured for 2½ hours. With respect to the improvement in mechanical properties, it behaved as if it had undergone "after-vulcanization," concerning the nature of which mention has already been made in another connection (p. 282). This may lead to an improvement, as is well known, but it may also lead to a reduction in mechanical properties. This must be taken into consideration in the phenomenon of the aging of rubber products.

Stevens carried out these aging experiments not only with crepe, but also with smoked sheets. Since the observations made on the latter are similar in general to those already described, there is no need of repeating them. Later Stevens [70] extended his investigations to include the influence of temperature on the aging of rubber products, and it was shown that the depreciation at 28° C. was distinctly more pronounced than at 11.5° C. Furthermore, it was clearly shown that the course of the aging can be followed much better by the tensile strength curve than by the vulcanization coefficient, since the latter does not change to so great an extent as the mechanical properties. This was especially apparent from experiments with different kinds of rubber. Thus the chemical processes of "after-vulcanization" not only play a part in aging, but changes also take place which involve the physical state of the rubber, i. e., its degree of aggregation. When Stevens continued these aging experiments with different kinds of rubber up to a period of two years, and every ten weeks determined the vulcanization coefficients, the elongation, and the strength, he found that the tensile strength of all the samples with a coefficient appreciably above three increased during the first few weeks, but then very rapidly decreased. On the contrary vulcanizates with from 2.8 to 3.4 per cent of combined sulfur, showed increasing strength for nearly one year, and the tensile curve then fell off only gradually. The tendency for "after-vulcanization" and for aging thus depends on the degree of vulcanization of the rubber. The higher the original vulcanization coefficient, the greater the average increase in combined sulfur. For example, during a certain aging period, the increases amounted to the following:

Average coefficients	Increase
2.53	0.02% sulfur
3.43	0.10% sulfur
4.55	0.25% sulfur
5.69	0.51% sulfur

[70] *J. Soc. Chem. Ind.*, **37**, 280T (1918).

Later Stevens [71] proved that the aging of rubber goods is also dependent upon the humidity of the surrounding atmosphere. After six months standing in air which was saturated with moisture, no deterioration could be observed even at tropical temperatures. This result coincides with the findings which were made earlier at the Materialprüfungsamt in Berlin-Dahlem, while "after-vulcanization" was being studied (*see* p. 282). The aging of rubber products is dependent upon the climatic conditions. Consequently these products keep well even at tropical temperatures, provided the atmosphere has a sufficient moisture content.

DeVries and Hellendoorn [72] obtained results similar to those of Stevens on aging rubber mixes which contained 92.5 per cent of rubber and 7.5 per cent of sulfur. With one sample, which was cured for 90 minutes at 148° C., the tensile strength, even after aging for 2½ years at the tropical temperature of 27° C., was higher than shortly after completion of the vulcanization. On the other hand, the strength of a sample, vulcanized for 125 minutes at the same temperature, depreciated in the same period from 130 kg./cm.^{2} to 90 kg./cm.^{2}. DeVries [73] also came to the conclusion that the coefficient of vulcanization is not the only deciding factor in the aging of rubber products, for it had not risen to the extent that was to be expected from the changes in mechanical properties. In this connection, Geer and Evans [74] had already expressed the view that, besides the increase in vulcanization coefficient, a chemical action of the oxygen of the air is also responsible for the phenomenon of "after-vulcanization" and aging. This view is corroborated by the observations of Spence (*see* p. 283), whose results have already been extensively discussed in other connections. He has shown that with samples which tend to age poorly, there is, in the first place, a decided increase in the acetone-soluble constituents, in addition to the increase in combined sulfur. It was Stevens,[75] however, who obtained direct proof that the oxygen of the air takes part in the phenomenon of aging of vulcanized rubber. He found that the weight increases on storing in the air and that the increase is ascribable to oxygen absorption by the rubber. He further confirmed the long-known fact that vulcanized rubber, which has been extracted with acetone, ages or increases in weight more rapidly than unextracted rubber. The resins thus protect against oxidation. He also established the fact that volatile sulfur compounds are formed during aging. The latter observation was corroborated by investigations of Eaton and Day,[76] which they undertook in order to ascertain the changes in chemical composition of vulcanizates during aging. They started with a mixture consisting of 90 parts of rubber and 10 parts of sulfur. Samples of this composition were vulcanized for different lengths of time and aged, in one case, in the form of thin sheets; in another case, in a finely ground condition. The ground material was in one case spread out on a watch-glass, and in another case placed in a test tube. Samples which had been vulcanized for nine hours showed, after nine months aging in air in the finely divided condition on the watch glass, a weight increase of 25 per cent; in the test tube an increase of 39.4 per cent. It thus appeared that volatile compounds were formed on aging, which on the watch glass, i.e., open to the air, could more readily volatilize than in the test tube experiment. The weight increase was observable also in the sample vulcanized for only three hours, while the increase in the sample cured for

[71] *J. Soc. Chem. Ind.*, **39**, 251T (1920).
[72] *India Rubber J.*, **61**, 87 (1921).
[73] *India Rubber J.*, **53**, 101 (1917).
[74] *India Rubber World*, **55**, 127 (1916).
[75] *J. Soc. Chem. Ind.*, **38**, 192T (1919).
[76] *J. Soc. Chem. Ind.*, **38**, 339T (1919).

1¼ hours, which had approximately the optimum degree of vulcanization, was 6 per cent on the watch-glass and in the test tube, surprisingly, only 3.6 per cent. The formation of volatile products thus appears to be involved particularly in over-vulcanized samples. When Eaton and Day investigated the aged samples more closely, they found that the oxidized material consisted largely of acidic, water-soluble compounds. The sample which had been vulcanized for nine hours yielded, for example, 23.4 per cent of water-soluble substances, which contained 0.45 per cent of sulfur.[77] The acidity of this water-soluble portion calculated as sulfuric acid was 2.68 per cent. According to this observation, the sulfur is also involved in the aging. This is not surprising, for it is known that hard rubber on standing in the air and light becomes covered with a film of sulfuric acid. In the case of soft rubber, the sulfuric acid formed may then cause further damage. Spence[78] had already made mention of the fact that even small amounts of sulfuric acid harden vulcanized rubber extraordinarily quickly if the rubber is not specially protected by adding materials which repel water or neutralize the acid. He also found that traces of sulfuric acid had a disaggregating effect on the rubber hydrocarbon, especially in the case of crude rubber. That disaggregated rubber is especially susceptible to oxidation is well known. In this connection, the experiments of F. Kirchhof[79] should also be mentioned. According to these, the sulfuric acid perhaps changes the substances present in the rubber which protect it against oxidation, so that they lose their protective influence.

The role of oxygen as the active agent in the aging of rubber has been very clearly shown by Marzetti.[80] Experiments conducted at 75° C. proved that aging is a physical process which takes place in an atmosphere of oxygen, but not in carbon dioxide. Even though the vulcanizate takes up only 1 per cent of oxygen, this amount is sufficient to affect the physical properties very definitely and to cause the material to deteriorate rapidly. The aging also proved to be dependent upon the quality of the crude rubber and the kind of ingredients which it contained.

The extensive studies by F. Kirchhof[81] on the oxidation of the rubber hydrocarbon over a period of years, call for discussion. As early as 1913, he drew the following conclusions[82] from investigations which he had carried out on acetone-extracted soft rubber vulcanizates, in a current of air at 95° C.:

1. Oxidation is dependent upon the degree of vulcanization. Under-vulcanized samples oxidize more slowly and over-vulcanized samples more rapidly than those that have been normally vulcanized.

2. At elevated temperatures, the oxidation takes place with the simultaneous splitting off of water, so that the resulting increase in weight of the samples consists of the difference between the total amount of oxygen taken up and that split off as water. This cleavage of water involves the sulfuric acid, formed as a result of the partial oxidation of the combined sulfur. The acid has a dehydrating action, especially at higher temperatures, on the oxidation products of the rubber.

3. With respect to physical and chemical behavior, the oxidation products of rubber may be classified into the three following groups:

(a) acetone-soluble materials of yellowish to reddish-brown color, empyreumatic-aromatic odor and strongly acidic character.

(b) materials soluble in alcoholic-potash, of similar behavior, but of weaker acidic character.

(c) dark brown, amorphous substances, insoluble in all organic solvents.*

[77] Calculated on the original rubber sample.
[78] *Kolloid-Z.*, **4**, 70 (1909).
[79] *Kautschuk*, **3**, 239 (1927).
[80] *Giorn. chim. ind. applicata*, **5**, 122-24 (1923) March
[81] *Kautschuk*, **3**, 256 (1927).
[82] *Kolloid-Z.*, **13**, 49 (1913).
* Translator's Note. According to J. W. Temple, S. M. Cadwell and M. W. Mead, Jr.

The sulfur, chemically combined during vulcanization, goes, for the most part, into the oxidation products, where it appears to be present chiefly in the soluble portions in the form of sulfo-acids or similar compounds. Part of the sulfur volatilizes as SO_2 or SO_3.

Later Kirchhof [83] established the interesting fact that the acetone- and alkali-soluble oxidation products of vulcanized rubber are identical with the analogous products which are formed (along with cyclorubber) by the action of concentrated sulfuric acid on crude rubber solutions. Recently,[84] he also performed experiments with different types of vulcanizates. Samples of known composition, after being tested for mechanical properties, were subjected, in the form of very thin sheets, to oxidation at 70° C. in thermostats. Some of the experiments were conducted in oxygen and some in a current of air, on samples that had been acetone-extracted as well as on samples in their original state. The rubber mixings used had the following compositions:

Mixture A	Per cent	Mixture B	Per cent
Ceylon Crepe	97.0	Para	90.0
Sulfur	1.2	Sulfur	8.0
Zinc oxide	0.6	Magnesia	0.4
Accelerators	1.2	Softener	1.6
	100.0		100.0

Mixture A contains equal amounts of two undivulged organic accelerators. Since decidedly less sulfur need be added to a mixture containing such substances, than to one in which they are absent, no "after-vulcanization," or only a minimum of "after-vulcanization," can occur. Real danger of premature deterioration of the vulcanizate is thus largely avoided. The favorable influence of accelerators had already been pointed out by K. Gottlob and F. Hofmann,[85] as well as by P. Schidrowitz and J. R. Burnand [86] and by D. Spence.[87] *

Kirchhof vulcanized the above mixture in sheets 5 mm. thick for 15, 30, 60, and 90 minutes at 143° C. in a press. The mechanical properties of the vulcanizates were determined after they had stood for 48 hours (cross-sectional area of the ring 0.25 cm.^{2}, diameter 25 mm.). (*See* Table 22.)

A vulcanization period of 30 minutes produced the optimum properties in the case of the low-sulfur crepe mixture, while the optimum in the case of the high-sulfur Para mixture was found to be at about 100 to 110 minutes

[*Ind. Eng. Chem., Anal. Ed.*, **2**, 377 (1930)]. the early stages of the oxidation of vulcanized rubber are accompanied by the formation of levulinic aldehyde or other compounds detectable by the pyrrole test with pine splints and hydrochloric acid. This test fails, however, after oxidation has progressed to the point where physical deterioration sets in. B. Dogadkin and W. Balandina [*Kautschuk*, **9**, 146-8 (1933)] have found that the aqueous extracts of pale crepe or smoked sheets which have been exposed to ultra-violet light or milled for a short time on cold rolls, reduce alkaline gold chloride solutions with the formation of colloidal gold. The reducing power of the extract begins to decrease, and its specific conductivity begins to increase, after about 30 minutes of either treatment.—C. S. D.

[83] *Kolloid-Z.*, **30**, 176 (1922).

[84] *Kautschuk*, **3**, 256 (1927).

[85] K. Gottlob, "*Technologie der Kautschukwaren*," 2nd ed., p. 176, Vieweg u. Sohn, Braunschweig, **1925.**

[86] *J. Soc. Chem. Ind.*, **40**, 269T (1921).

[87] *India Rubber World*, **57**, 281 (1918).

* Translator's Note. The appearance of several recent papers [L. B. Cox and C. R. Park, *Ind. Eng. Chem.*, **20**, 1088 (1928); R. P. Dinsmore and W. W. Vogt, *Trans. Inst. Rubber Ind.*, **4**, 85 (1928); W. C. Davey, *ibid.*, **4**, 493 (1929); **5**, 386 (1930); **6**, 202 (1930); G. Martin and R. Thiollet, *Rev. gén. caoutchouc*, (8) **75**, 133-6 (1931)] has indicated a revival of interest in this subject. In this connection, N. A. Shepard and J. N. Street [*Ind. Eng. Chem.*, **24**, 574 (1932)] have found definite tendencies toward better aging of vulcanizates when relatively low temperatures were used in curing.—C. S. D.

TABLE 22.—*Experiments on the Influence of Vulcanization Time (Kirchhof).*

Mixture	Cure (min.)	Coefficient of vulcanization	Tensile strength kg./cm.²	Elongation at break. Orig. length = 100%	Evaluation * Figure (cm.²)
A	15	—	75.6	1270	22.8
	30	1.6	64.4	1310	25
	60	—	49.8	1386	21
B	15	1.7	26.6	1360	12
	30	2.4	44	1334	23
	60	3.8	72.4	1330	30
	90	4.9	97.6	1260	35.3

* These values have been obtained by means of a planimeter, and refer therefore only to a cross-section of 0.5 cm². Translator's Note. Probably the area under the stress-strain curve.—N. A. S.

of cure. As already stated, samples of these vulcanizates, after extraction, were subjected to oxidation in a stream of pure dry oxygen at 70° C. From the oxidation chamber the gas was passed through two calcium chloride U-tubes and then through a tube containing soda-lime. The results of the experiments with the 15-minute cure of Mixture A and the 90-minute cure of Mixture B are given in Table 23.

TABLE 23.—*Oxidation Experiments on Vulcanized Rubber (Kirchhof).*

		Increase in weight					
	Period of oxidation	Of the samples		Of the calcium chloride tubes		Of the soda-lime tubes	
Mixture	(hours)	grams	per cent	grams	per cent	grams	per ce
A 15	46	0.007	0.35	0.0	—	—	—
	92	0.052	2.7	0.025	1.28	0.010	—
	155	0.209	10.7	0.050	2.6	0.024	—
	203	0.340	17.4	0.100	5.0	0.033	—
	225	0.358	18.3	0.120	6.0	0.043	2.2
	272	0.371	19.2	0.153	7.65	—	—
B 90 (1)	44	0.210	11.0	0.070	3.7	—	—
	92	0.277	14.5	0.130	6.8	0.027	1.4
	140	0.292	15.25	0.200	10.4	0.044	2.3
	188	0.302	15.8	0.230	12.1	0.052	2.7

These again show the well-known dependence of the speed of oxidation on the degree of vulcanization. Mixture A, vulcanized to a low state of cure, can take up oxygen only after an induction period of about 48 hours (disaggregation), which then continues linearly for a period of about 200 hours, attaining a maximum value. The oxidation of Mixture B proceeds in an entirely different manner. It sets in immediately after the start of the experiment and reaches a point beyond which there is only a small increase in weight, in about half the time required in the case of Mixture A. The maximum amount of oxygen absorbed was about 3 per cent lower in the case of the high-sulfur Mixture B than in the case of Mixture A. This appears to be in accord with the view that in vulcanization the double bonds in the rubber become saturated with sulfur. However, this difference in the maximum oxygen absorption appears to be dependent upon too many factors to permit of drawing broad conclusions.

In an experiment conducted by Kirchhof in a more dilute stream of oxygen, the oxygen absorption of the different vulcanizates of Mixture B

reached a peak at a figure about half the value calculated on the basis of its rubber content, as Table 24 shows.

TABLE 24.—*Experiments by Kirchhof on the Oxygen Absorption of Vulcanized Rubber.*

Period of oxidation (hours)	Weight increase of the extracted samples (per cent)			
	B 15	B 30	B 60	B 90
48	1.2	1.68	3.2	5.4
96	5.6	6.20	9.6	9.7
116	8.0	8.70	10.3	10.2
164	10.5	11.10	10.7	11.2
212	10.6	12.1	12.3	11.8

This phenomenon, already observed earlier by Kirchhof, is certainly attributable to the splitting off of water which simultaneously takes place at the higher temperature through the condensing action of the sulfuric acid formed by the oxidation of the sulfur. At the same time a cyclization (*see* p. 189) of the rubber might also take place through the action of the sulfuric acid, which brings about a reduction in the number of double bonds. Such cyclization appears to be involved, according to the view of Kirchhof, in all such cases, where, as the result of the formation of relatively large amounts of sulfuric acid, the vulcanizates harden and become brittle without a noticeable increase in weight. Polycyclo-rubber is an amorphous, white powder, which has no similarity to rubber. Thus the sulfur has marked significance not only in the vulcanization itself but also from the standpoint of the later fate of the vulcanizate. It itself is oxidized and is transformed partially into volatile compounds. Part of it goes into the acetone-soluble and part into the acetone-insoluble, amorphous portions of the rubber in a more or less oxidized condition. It is probably for this reason that more highly vulcanized samples always show a greater increase in weight than samples in a lower state of vulcanization. This susceptibility of the combined sulfur to attack by oxygen, is manifest in the increasing tendency towards oxidation with increasing coefficient of vulcanization. This readily explains the favorable effect of organic accelerators.

In oxidation experiments which Kirchhof carried out with the same vulcanizates in a stream of air at 70° C., he obtained the results in Table 25.*

TABLE 25.—*Oxidation Experiments in a Stream of Air at 70° C. (Kirchhof).*

Period of oxidation (hours)	Weight increase of the samples in per cent of extractable substances			Appearance of the oxidized substances
	A-15	A-30	A-60	
96	3.9	4.2	4.7	Bright yellow
192	6.9	7.2	7.9	Dark yellow
336	11.9	13.3	13.9	Brownish color
352	17.2	18.0	19.0	Dark brown
Acetone extr. (%)	34.0	35.1	35.3	

Translator's Note. In an examination of the rate and extent of oxygen-absorption by vulcanized rubbers, G. T. Kohman [*J. Phys. Chem.*, **33**, 226-43 (1929); *Rubber Chem. Tech.*, **2**, 390 (1929)] has traced the parallelism between physical deterioration and the absorption of oxygen and of ozonized oxygen. I. Williams and A. M. Neal [*Ind. Eng. Chem.*, **22**, 874 (1930)] have found that the concentration of oxygen dissolved in vulcanized rubber in contact with air at 70° C. or in contact with oxygen itself at 29° C. at atmospheric pressure is less than that required for uniform oxidation at the maximum rate.—C. S. D.

The acetone extract shows a linear relationship with the increase in weight, and likewise shows the dependence of the latter on the degree of vulcanization.* The oxidation of rubber is thus similar to the vulcanization of rubber, for the increase in weight during oxidation at a given temperature is dependent to a large extent upon the concentration of the oxygen. In a stream of air at 70° C., the behavior is similar to that in an unaccelerated vulcanization with 8 to 10 per cent of sulfur, while the oxidation in a stream of oxygen is comparable in rate to that in the vulcanization of a mixture of high sulfur content. Again, the principal relationships which hold in vulcanization in the presence of organic accelerators are comparable to those encountered in oxidation in ultra-violet light. On the basis of these experiments, Kirchhof has come to the conclusion that the velocity of oxidation in a current of oxygen (from about the hundredth hour on) is approximately double that in a stream of air (at 70° C. in both cases), while the oxidation in ultra-violet light at 40° to 50° C. in air is about three times as great as in the same medium in the dark in the Geer oven (*see* p. 618).

The influence of ultra-violet light on the aging of vulcanized rubber was investigated by Takayi Yamazaki.[88] In this case it was compared with the action of sunlight. Again it was shown that the amount of the vulcanizate soluble in acetone increased both in the sunlight and in ultra-violet light† in the presence of air and of oxygen, while this was not the case in an atmosphere of carbon dioxide. At the same time, the free sulfur content of the samples dropped. "After-vulcanization" also set in, which, according to Helbronner and Bernstein,[89] was to be expected. These investigators brought about the vulcanization of rubber-sulfur cements at room temperature under the influence of ultra-violet rays. In the experiments of Yamazaki, the intensity of the changes in the samples during the same periods was dependent on the degree of vulcanization of the samples, and on the kind of rubber, as well as on the conditions under which the vulcanizates were investigated. Acetone-extracted mixes aged more rapidly than samples which were not extracted. In vulcanizates containing the same kind of rubber, the velocity of oxidation increased with the content of combined sulfur and, in the case of Para rubber, was approximately four times as great in the extracted condition as in the unextracted. The oxidation took place about three times as fast in the vulcanizate containing Ceylon crepe as in that containing Para. In the case of the crepe, however, the difference in weight increase between the extracted and unextracted samples was only about half as great as in the case of the Para rubber. In Kirchhof's[90] opinion, this is chiefly attributable to the different translucency of these types of rubber, which is a function of their respective colors. In experiments which he undertook with sheets of unvulcanized Ceylon crepe and smoked sheets of

* Translator's Note. In an examination of the crease in weight and increase in acetone-extractable content during oxidation has been shown to be less simple than is indicated here, according to more recent work [A. van Rossem and P. Dekker, *Kautschuk*, **5**, 13-21 (1929); W. C. Davey, *Trans. Inst. Rubber Ind.*, **4**, 493-8 (1929); T. Yamazaki and K. Okuyama, *J. Soc. Chem. Ind., Japan, Suppl.*, **32**, 368-70B (1929); **33**, 68-72B (1930), *Rubber Chem. Tech.*, **3**, 378 (1930)].—C. S. D.

[88] *J. Soc. Chem. Ind. Japan*, Suppl. (1926); **30**, 209B (1927).

† Translator's Note. B. B. Evans [*Trans. Inst. Rubber Ind.*, **5**, 442-9 (1930)] found that ultra-violet light did not simulate sunlight in its effect on the checking of bent vulcanizates.—C. S. D.

[89] *Caoutchouc & gutta-percha*, **12**, 8720 (1915).

[90] *Kautschuk*, **3**, 239 (1927).

the same thickness, he found that the originally large difference in the translucency appeared to be lessened after three days radiation with ultra-violet light, since the crepe had become more opaque as the result of the formation of yellow oxidation products. Thus rubber itself produces among its oxidation products a material which protects it against light, and which progressively retards the further action of the light and thus of the oxygen. Kirchhof makes further mention of the fact that the differences in the velocity of oxidation in ultra-violet light, between extracted and unextracted vulcanizates containing the same kind of rubber and vulcanized in the same manner, appear also to be connected with the way in which the sulfur is linked. Thus it had already been recognized that photographs can be taken in ultra-violet light of pieces of unvulcanized, but not of vulcanized rubber, since the latter, i.e., vulcanized rubber, completely absorbs ultra-violet light. Then H. Green [91] found that pure carbon disulfide transmits ultra-violet light of 2750Å, but that this is no longer the case when sulfur is dissolved in this liquid. He used this phenomenon in studying the vulcanization of latex, since in this way it can be determined whether the sulfur is in solution or in chemical combination. Kirchhof thinks that because of the opacity of vulcanized rubber to ultra-violet light, he is correct in concluding that the lesser tendency of unextracted vulcanized rubber to oxidation in light is due partly to the strong absorptiveness, especially for light of short wave length, of the free (colloidal) sulfur still present.* This gives an explanation for the view held by practical rubber men, that moderately bloomed rubber goods in general age better than those which do not bloom. The microscopically thin layer of sulfur forms a distinct protection against light for the rubber surface below it, but this certainly cannot permanently prevent the deterioration of the vulcanizate.†

With respect to the chemical aspects of photo-oxidation, Kirchhof points out the formation of peculiar smelling, partly water-soluble, oxidation products, which are attributable to the primary formation of peroxides or ozonides. The characteristic difference between oxidation in a stream of oxygen in ultra-violet light and in the dark consists in the immediate beginning of the oxidation in the first case, in contrast to the occurrence of an induction period in the dark, when samples of the same degree of vulcanization are used. Since there is practically no splitting off of water in the case of oxidation in ultra-violet light at 40° to 45° C., Kirchhof was able to show that the weight increase in irradiated vulcanizates comes to a standstill much sooner than would be calculated for the formation of C_5H_8O. According to his views, this can only be explained through rearrangement or cyclization, in which some double bonds in the rubber disappear. He also observed that only about half of the oxidation products had become acetone-soluble. According to him, this observation likewise supports the view that the rubber hydrocarbon has changed to a large extent into insoluble polymers (rear-

[91] *Ind. Eng. Chem.*, **17**, 802 (1925).

* Translator's Note. More recently, F. Kirchhof [*Caoutchouc & gutta-percha*, **26**, 14,501-3 (1929)] has described the use of photographic observations with ultra-violet light in determining the penetration of oxygen. A change in physical structure during aging has been followed by another optical method in the work of B. L. Johnson and F. K. Cameron [*Ind. Eng. Chem.*, **25**, 1151 (1933)]. They have determined, by means of x-rays, the elongation required to cause "fibering" in strips of vulcanized rubber. The minimum elongation is increased by aging. Surprisingly, it is not affected by the antioxidant phenyl-beta-naphthylamine.—C. S. D.

† Translator's Note. However, T. Yamazaki and K. Okumura [*J. Soc. Chem. Ind., Japan, Suppl.*, **35**, 265-6B (1932); *Rubber Chem. Tech.*, **5**, 655 (1932)] found no correlation between free sulfur and the deterioration of stocks vulcanized in the presence of diphenylguanidine or diorthotolylguanidine.—C. S. D.

rangement products or cyclorubbers) or their insoluble oxidation products. Thus, as the result of the simultaneous rearrangement of part of the rubber hydrocarbon into less unsaturated isomers, less oxygen is taken up in oxidation in ultra-violet light than in oxidation in the dark. Thus rubber protects itself almost automatically from further oxidation by changing, first at the surface, into an isomeric body which makes the further penetration of light and oxygen difficult.*

Besides the phenomena of deterioration of rubber goods already described, which lead to a hard and brittle condition, cases are sometimes observed with weakly vulcanized, and especially with cold vulcanized rubber, in which a softening takes place prior to hardening and becoming brittle. This is very similar to the development of stickiness or "tackiness" in raw rubber (*see* p. 148 and the following pages). According to D. Spence,[92] this is attributable to disaggregation of the rubber brought about partly by heat and partly by traces of sulfuric acid, the rubber in this condition being especially susceptible to oxidation. The true cause of this condition, which frequently occurs only a short time after the vulcanization of rubber products, is the catalytic action of small amounts of the salts of the heavy metals present in the rubber mix. This was recognized over 40 years ago by W. Thomson and F. Lewis.[93] They sprinkled thin sheets of cold vulcanized rubber with metal filings and heated them for 10 days at 60° C. Copper was found to be especially deleterious. Further experiments showed that copper salts, vanadium chloride, silver nitrate, and manganic oxide (Mn_2O_3) also bring about complete disintegration, and that the action of metals appears to be especially powerful in mixings containing oils. Later C. O. Weber [94] called attention to the harmful effect of small amounts of copper present in textile fabrics used in the manufacture of rubberized goods. He also proved that with the same content of copper in the fabric, the damage is considerably greater in cold vulcanized than in hot vulcanized rubberizing. Weber attributed this difference to the formation in cold vulcanized goods of cupric chloride, which is known to have a powerful action as an oxygen carrier. On the other hand, copper sulfide formed during hot vulcanization is in itself harmless and only does harm if it is converted by oxidation into copper sulfate, which acts as an oxygen carrier. Kirchhof [95] supplemented this finding of Weber by showing that as little as 0.1 per cent of copper in the fabric will cause definite damage† (*see* Fig. 193).

The observations of Thomson and Lewis on the destructive effect of manganese oxides on rubber was later confirmed by L. E. Weber, as well as

* Translator's Note. This conclusion is supported by the work of H. A. Depew [*Ind. Eng. Chem.*, **24**, 992 (1932)] who noted the diminishing rate of deterioration of thick layers with advancing periods of aging. On the other hand, it has been found [R. T. Vanderbilt Co., *Vanderbilt News*, **2**, No. 4, 20-4 (1932); *Chem. Abstracts*, **26**, 5451 (1932)] that the rate of deterioration in the oxygen bomb or in the Geer oven is practically indipendent of thickness. Moreover, E. P. W. Kearsley [*Rubber Age (N. Y.)*, **27**, 649 (1930)] from experiments on the testing of vulcanized rubber in contact with ozone, pointed out that oxidation is a secondary effect in the action of light.—C. S. D.

[92] *Kolloid-Z.*, **4**, 70 (1909).

[93] *Chem. News*, **64**, 169 (1891); *Gummi-Ztg.*, **5**, No. 8, p. 7 (1891); **6**, No. 5, p. 2 (1891); *J. Soc. Chem. Ind.*, **10**, 712 (1891); *Mem. Manchester Lit. Phil. Soc.*, (4), **4**, 266 (1891) (original reference).

[94] *J. Soc. Dyers & Colorists*, (5) **16**, 98 (1900); *J. Soc. Chem. Ind.*, **19**, 546 (1900).

[95] *Kautschuk*, **3**, 256 (1927).

† Translator's Note. F. Kirchhof [*Kautschuk*, **8**, 6-8 (1932)] has also reported on the combined effect of sulfur and copper upon some inner tubes. These tubes, which were so vulcanized that one bloomed while the other remained free from bloom (by overcuring), were both marked with a bronze paint. After six years the non-blooming tube was deeply cracked. It was found to contain 0.21 per cent of $CuSO_4$, while the blooming tube, which was not cracked, and which contained three times the concentration of total copper as did the other, was found to have but 0.03 per cent of $CuSO_4$. However, the higher state of cure, in the case of the non-blooming sample, undoubtedly influenced the results.—C. S. D.

by Bruni and Pelizzola.[96] The latter authors found that 1 per cent of colloidal manganese dioxide decomposed rubber within a few weeks. F. Frank [97] was the first to call attention to the bad influence of organic ferric salts and inorganic ferrous compounds. According to Kirchhof,[98] the rapid aging of rubber mixings containing ferric oxide, as compared with those containing antimony pentasulfide, is attributable to the presence of organic or inorganic iron salts.*

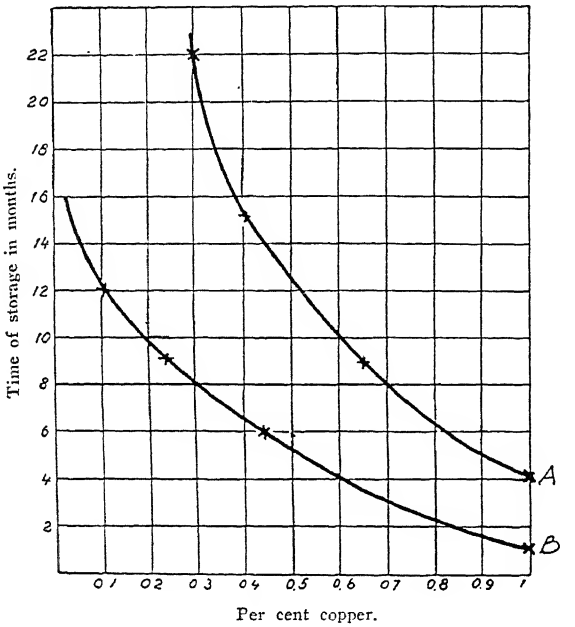


Figure 193 — Influence of copper on the aging of vulcanized rubber.

The points on the curves represent the inception of significant decomposition.

A. Hot-vulcanized rubberized fabric (Para rubber and sulfur).

B. Cold-vulcanized rubberized fabric (Para rubber).

The investigations of H. Rimpel [99] and M. Levin [100] on the effect of rosin in rubber mixes, give definite information concerning the role played by the rubber resins in the deleterious action of metals. These resins, according to the more recent information, consist partly of free fatty acids. As is well known, rosin itself acts as an oxygen carrier; this property is appreciably intensified if the abietic acid has the opportunity of uniting with metals such, for example, as lead, copper, and manganese, to form resinates. These resinates, the so-called "siccatives" or "drying" agents, are very well known to be exceptionally powerful oxygen carriers. H. Rimpel was able to show, however, that the deleterious effect does not necessarily take place, for rubber mixings containing 15 to 25 per cent of rosin showed no trace of deterioration after 290 hours aging at 70° C. According to W. Esch,[101] rubber mixes containing rosin age satisfactorily provided well dried material is used in making them. Rosin containing moisture has a bad effect. In dry rosin, the

[96] *India Rubber J.*, **62**, 101 (1921).
[97] *Dt. Luft.-Ztg.*, **52** (1912); *Gummi-Ztg.*, **26**, 801 (1912); *J. Soc. Chem. Ind.*, **31**, 348 (1912).
[98] *Kautschuk*, **3**, 256 (1927).
* Translator's Note. J. W. Ayers [*Ind. Eng. Chem.*, **24**, 320-3 (1932)] has demonstrated the deleterious effect of an iron oxide pigment which contains ferric sulfate.—C. S. D.
[99] *Kautschuk*, **2**, 95 (1926).
[100] *India Rubber World*, **75**, 83 (1926).
[101] *Gummi-Ztg.*, **40**, 2697 (1926).

abietic acid is in the form of its anhydride, while the product which is not well dried, contains the free acid, which can form siccatives. Moreover, it is now known that basic substances like lead oxide, for example, can cause the decomposition of the glycerides of fatty acids. In such cases lead soaps are formed, which are likewise known to be powerful oxygen carriers. The fact, mentioned above, that certain metals or their compounds are especially active in mixtures containing oils, can be similarly explained.*

Comprehensive studies on the deleterious action of heavy metal compounds on fabrics rubberized with pure Para, and on mixtures which contain white and brown factice, were undertaken by F. Kirchhof.[102] These led to the following results:

1. Whether the heavy metal is in a soluble or insoluble form, and whether it is present alone or in combination with other heavy metals, must be known.
2. The heavy metals differ in their action on rubberized products. The products become sticky in the presence of ferric, chromic, and lead acetates, stannic chloride, zinc sulfite, copper and ferrous sulfates. They become brittle in the presence of stannates, ferric chloride, rosin, and the resinates of manganese and lead.
3. The action of these heavy metal compounds may be placed in approximately the following order of decreasing intensity:
   (a) In the presence of water-soluble metallic compounds:
      (1) Copper salts with ferric salts.
      (2) Copper sulfate.
      (3) Ferric salts with sodium stannate.
      (4) Stannous chloride.
      (5) Copper-iron cyanide (Hatchett brown).
      (6) Zinc bisulfite (Dekrolin).
      (7) Ferric acetate.
      (8) Sodium stannate.
      (9) Chromic acetate.
      (10) Chromic bisulfite.
   (b) In the absence of water-soluble metallic compounds (hydroxides, basic salts), but in the presence of white factice:
      (1) Basic ferric compounds.
      (2) Copper.
      (3) Tin.
      (4) Manganese.
      (5) Lead compounds, rosin, basic zinc compounds.

   According to Kirchhof's views, these compounds form chlorides with traces of hydrochloric acid which are split off, and these have a depolymerizing action or act as oxygen carriers. In the case of rosin, this action is produced by the rosin acids.
4. Lead and zinc chromates, as a result of their difficult solubility, have little or no action.
5. The following have a very powerful and destructive action in ultra-violet light, producing tackiness:
   (a) Stannous chloride.
   (b) Manganese compounds in the presence of rosin.
   (c) Ferric chloride.

   On the other hand, sodium stannate, sodium stannate with chromic acetate, potassium dichromate, and lead chromate have a definite protective action. According to Kirchhof, this is attributable to the action of these compounds in disturbing or preventing the formation of ozone, as has been shown by I. Williams[103] in the case of copper sulfate.

The metal compounds used in the experiments may be partly in the form of mordants in the fabric and remain there, partly absorbed.

* Translator's Note. Litharge, for which a protective action against aging has been claimed, has been found actually to increase the rate of oxidation of vulcanized rubber, while decreasing slightly its rate of physical deterioration [C. Dufraisse and N. Drisch, *Rev. gén. caoutchouc*, (8) **77**, 5-6 (1931); *Rubber Chem. Tech.*, **5**, 301 (1932)].—C. S. D.

[102] Kautschuk, **3**, 256 (1927).

[103] *Ind. Eng. Chem.*, **18**, 367 (1926).

F. Kirchhof attempted to explain the action of metal compounds in the following manner:

(a) Water-soluble heavy metal compounds (chlorides, sulfates, sulfites, and acetates) act chiefly through the formation of metallic soaps of the resin acids of the rubber, whereby traces of free, strong acids are formed, which are known to have a depolymerizing (disaggregating) effect on cold vulcanized rubber, producing tackiness.

(b) Water-insoluble metallic compounds (oxides, hydroxides, and sulfides) may be transformed, on the one hand, by the acidic part of the rubber resins (organic fatty acids) into easily soluble compounds, and, on the other hand, by traces of hydrochloric acid split off from cold vulcanized rubber or by sulfuric acid formed by oxidation, into water-soluble substances, which then may act as indicated under (a).

Then the oxygen-carrier effect of the metallic soaps formed comes into play, which is entirely analogous to the drying action in varnishes, and which leads to the hardening and embrittling of rubberized products.

In the same piece of work, F. Kirchhof also points out the rapid aging which is often observed in the case of gas black mixes, and explains it as being due to the fact that oxygen, condensed on the surface of the black, as the result of adsorption, comes into intimate contact with the rubber (because of the large surfaces of contact of the black and rubber). This results in a correspondingly rapid, even if quantitatively small, oxidation, which, however, leads to relatively large physical changes.

Summing up, it may be said that the aging of rubber products consists primarily in an oxidation of the vulcanized rubber. It is only natural that with this knowledge endeavors were made to avoid this undesirable phenomenon as far as possible. Much was accomplished in this direction by the discovery of organic accelerators through the application of which it was possible to work with much less total sulfur in the rubber mixes than formerly. In this way, on the one hand, the danger of over-vulcanization and after-vulcanization was removed, both of which promote oxidation, and, on the other hand, the disaggregating action of heat on the rubber was substantially reduced. This action of heat likewise increases the tendency of rubber to oxidize. In this respect, rubber products manufactured with organic accelerators are very greatly improved. In addition, it was found that certain organic compounds had an inhibiting effect on oxidation of synthetic rubber (*cf.* p. 316). Non-volatile bases of the aromatic and heterocyclic series with two amino groups, or one amino and one hydroxyl group, proved most valuable. As a result of this observation, compounds like aldol-*alpha*-naphthylamine, for example, which offered considerable protection against aging when added to the rubber mix, were later discovered.

Thus paraminophenol* has been cited as of particular value in offsetting the effect of cuprous iodide in normally cured stocks [J. M. Bierer and C. C. Davis, *Trans. Inst. Rubber Ind.*, **3**, 151-84 (1927)]. Secondary amines have also been recommended in this connection [P. C. Jones and D. Craig, *Ind. Eng. Chem.*, **23**, 23-5 (1931)] while F. Kirchhof [*Kautschuk*, **6**, 119-20 (1930); **7**, 7-12 (1931); **9**, 70-2 (1933); *Rubber Chem. Tech.*, **4**, 239 (1931); **6**, 391 (1933)] has examined the direct action of cupric and other metallic salts as well as of light, on various antioxidants. C. Dufraisse and N. Drisch [*Rev. gén. caoutchouc*, (8) **71**, 9-24; **75**, 39-54 (1931)] have examined the effect of both positive and negative catalysts of autoxidation upon vulcanized rubber.

Hevea rubber is known to contain natural antioxidants, characterized as sterols and phytosterols [Bruson, Sebrell and Vogt, *Ind. Eng. Chem.*, **19**, 1187 (1927); (*see* also p. 165); H. F. Bondy, *Ber.*, **66**, 1611 (1933)]. These materials, as valuable as they

* Translator's note by C. S. D.

are in preserving crude rubber, retain little of their power after vulcanization. It has been necessary, as indicated above, to manufacture synthetic chemicals to take their place. The number of organic antioxidants now known is high. Surveys of this field have been made by Naunton [W. J. S. Naunton, *Trans. Inst. Rubber Ind.*, **5,** 317 (1930)], F. Jacobs [*Caoutchouc & gutta-percha*, **30,** 16548 (1933)] and others, among whom are W. L. Semon, A. W. Sloan and D. Craig [*Ind. Eng. Chem.*, **22,** 1001 (1930)] who have compared surface application of antioxidants vs. mill incorporation in rubber. A representative list of the better known compounds used extensively for preserving vulcanized rubber include the following:

Amino- or hydroxy-compounds.

Para-hydroxydiphenyl (Parazone)
Hydroquinone
Para-aminophenol
p, p'-Diaminodiphenylmethane (Resistox)
2,4-Meta-toluylene diamine.

Secondary amines.

Diphenylamine
o- and *p*-Ditolylamines (Age-Rite Gel)
Phenyl-alpha-naphthylamine (Neozone A)
Phenyl-beta-naphthylamine (Age-Rite Powder, Neozone D)
Phenyl-beta-naphthylnitrosamine.
Symmetrical di-beta-naphthyl-para-phenylenediamine (Age-Rite White)
Symmetrical diphenyldiamino-ethane (Stabilite)
2,4-Diaminodiphenylamine (Oxynone)

Condensation products of amines with carbonyl compounds, e. g.,

of aniline with acetaldehyde (V. G. B.)
of alpha-naphthylamine with aldol (Age-Rite Resin)
of aniline with acetone (Flectol-A)
of diphenylamine with acetone (B. L. E.)

In Kirchhof's [104] opinion, the action of such protective agents, which are designated as antioxidants or preservatives, is probably attributable, on the one hand, to the fact that they are reducing agents and, on the other hand, to the fact that they form, through their own oxidation, dyestuffs which protect the rubber against light and air.*

Artificial Aging and the Usual Procedures for Conducting It

Obviously endeavors were very early made to ascertain, in the shortest possible time, through some method or other of testing, whether an object made of soft vulcanized rubber would have a sufficiently long life. Experience had taught that the good properties of a mix, determined a short time after vulcanization, are no guarantee that these good properties will persist over a period of years. Since no, or at the most only highly approximate, indications concerning the stability of a type of soft rubber towards aging could be obtained from the composition of the mixing, methods have been worked out for effecting an artificial aging in a short length of time, with the expectation that such an artificial aging would reflect, proportionally shortened, the natural aging process.

[104] *Kautschuk*, **3,** 239 (1927).

* Translator's Note. Charles Dufraisse [*Rev. gén. caoutchouc*, (9), **85,** 4-10; **86,** 3-21 (1932); *Rubber Chem. Tech.*, **6,** 157, 566 (1933)] and F. Kirchhof [*Kautschuk*, **9,** 88, 106, 124 (1933)] have recently summarized the work in this field in support of their theory that the deterioration of vulcanized rubber is an autoxidation process. According to Dufraisse, rubber preservatives, for which he prefers the term "antioxygens" to the formerly used term "antioxidants," serve as anti-catalysts for autoxidation. However, H. S. Taylor [*Proc. Am. Soc. Testing Materials*, **32,** II, 1-34 (1932); *Rubber Chem. Tech.*, **6,** 211 (1933)], in discussing the deterioration and oxygen absorption of rubber refers simply to catalysts of acceleration, e. g., copper, and catalysts of retardation, e. g., amines.—C. S. D.

Rubber has been subjected to the many factors responsible for natural aging, such as oxygen, light, and heat, in some cases separately, and in others combined, and with intensities which are many-fold the natural intensities. It was hoped that there would be a conversion factor applicable to all different kinds of rubber products, which would permit of predicting the natural aging from the changes brought about by artificial aging, such, for example, as one day of artificial aging equalling one month of natural aging.

As soon as a new method of artificial aging appeared, which in the majority of cases consisted of a combination and variation of the three factors mentioned above (occasionally also with the application of the electrical discharge), very definite conversion factors were usually laid down. However, when a larger number of mixes were investigated, there was more conservatism. Aside from this fundamentally incorrect [105] assumption concerning artificial aging, quite often very elementary errors were made. It was, for example, asserted that the action of the mercury vapor light was similar to that of sunlight, only augmented. The action of the rays of short wavelength was thus decidedly overestimated.

The investigations of F. P. Jecusco [106] on the action of light, have been especially illuminating. Jecusco let filtered sunlight act for 24 hours on a vulcanized rubber-sulfur mixture containing 10 per cent of sulfur. In order to exclude the influence of heat, he kept the temperature of the test pieces below 32° C., by means of a ventilator. Jecusco separated the different rays into three groups; those which in 24 hours raised the tensile strength (infrared, red, yellow, and ultra-violet No. 8),[107] a second group (green No. 4 and No. 7, violet, and ultra-violet No. 13), which leave the tensile strength unaltered, and a third group (the entire visible spectrum, as well as the extreme red and blue) which reduce the tensile strength. Similar investigations have also been carried out by Takeyi Yamazaki.[108]

In view of the fact that conclusions concerning the course of natural aging can be drawn from the results of an artificial aging only in the case of mixes that have already been tested, and then only with considerable uncertainty, it seems advisable to make the procedure for artificial aging as simple as possible, even though natural aging conditions might be approached somewhat more closely through the use of a more complicated method.

In their own investigations, the authors have chiefly used dry heat, in their earlier work at 85° C., and later at 70° C. As a rule, an aging period of 7 days was employed, but, where necessary, even longer periods of time were used. More recently, a stream of oxygen was circulated around the test pieces.

In a similar manner, W. W. Evans [109] and W. C. Geer [110] have conducted artificial aging experiments on soft rubber samples. They hang a number of samples, already cut into test strips 3/32″ thick, in an oven at 160° F. (71° C.). In order to increase the amount of oxidation, the air in the oven is continuously replenished and circulated through a ventilator. The longest period of exposure in the oven was 14 days, but after about 3 days, some of the samples were taken out, in order to obtain an aging curve. The testing of the samples was conducted 24 hours after removal from the oven.

[105] In the field of paints, the organic components of which likewise tend to age rapidly, artificial aging methods have also, again and again, been set up and called "short or quick tests." *Cf.* A. Schob, *Farben.-Ztg.*, **31**, 2608 (1926).

[106] *Ind. Eng. Chem.*, **18**, 420 (1926).

[107] These numbers refer to Cambosco spectro-radioscopic glass filters.

[108] *J. Soc. Chem. Ind., Japan*, **30**, 209B (1927); **31**, 65B, 66-67B, 273B (1928); **32**, 367-368B (1929).

[109] *Proc. Am. Soc. Testing Materials*, **22**, Part II, 548 (1922); *Chem. Abstracts*, **16**, 4364 (1922).

[110] *India Rubber World*, **64**, 887 (1921).

A closer approach to the conditions in natural aging was attempted by J. M. Bierer and C. C. Davis [111] through the use of heat and oxygen at high pressure. They hoped to be able to reproduce in a few hours the aged condition that would result after years of natural aging. The samples to be artificially aged are placed in a bomb, which is heated to 60° C. and supplied with oxygen at a pressure of 20 atmospheres. Precautionary measures must be taken to prevent explosion which might occur because of too violent oxidation.

Even if these procedures for conducting artificial aging, which have just been mentioned, have the advantage of affecting the samples almost equally throughout their thickness, which is not the case in a procedure which utilizes light as the chief factor, it is obvious that, in leaving out so important a factor as light, this artificial aging must differ considerably from natural aging.

An artificial aging which includes the simultaneous action of both heat and the light of a mercury vapor light is applied for testing insulating tape.[112]

Since in many cases, time does not permit of letting natural aging run its course in order to determine the aging quality of a product, procedures for conducting an artificial aging have to be resorted to. It must be kept in mind, however, that in an appreciable percentage of the cases, the results run exactly opposite to those obtained in natural aging and that in the really comparable cases—and what is comparable and what is not, can unfortunately be known only when the results of natural aging are available—the results only roughly parallel those of natural aging.

The physical testing methods, by means of which the effects of aging (either natural or artificial) are determined, are the same as are used in testing the un-aged materials. In America, a simple flexing test is employed for determining the influence of different temperatures on the tendency of rubber and gutta-percha mixings to crack (a brittleness test).[113] This, in a certain sense, may also be called an aging test. Experience has shown that soft rubber under mechanical load (especially under strain) ages much faster than in an unstressed condition. This should be taken into consideration in carrying out investigations on natural and artificial aging.*

Special Tests

Testing of Soft Rubber Articles in Their Manufactured Form

General

The tests for determining the properties of soft rubber goods which have been described thus far give little or no consideration to the form or manner of application of the finished product. The greater the advance of knowledge of materials and of testing, the less dependent will methods of testing be on the form and size of a finished article. It often happens, however, that the

[111] *Ind. Eng. Chem.*, **16**, 711 (1924).
[112] M. Krahl, *Kautschuk*, **3**, 180 (1927).
[113] G. T. Kohman and R. L. Peek, *Ind. Eng. Chem.*, **20**, 81 (1928).
* Translator's Note. A. B. Kelly, B. S. Taylor and W. N. Jones [*Ind. Eng. Chem.*, **20**, 296-8 (1928)] as well as A. A. Somerville, J. M. Ball and W. H. Cope [*ibid.*, **21**, 1183 (1929)] have shown that stretched rubber deteriorates more rapidly in the Geer oven than does unstretched rubber. The cracking of vulcanized rubber in ozone or in sunlight occurs only when the rubber is in a stretched condition, according to F. H. Haushalter, W. N. Jones and J. W. Schade [*ibid.*, **20**, 300-2 (1928)], although O. Merz [*Kautschuk*, **8**, 73-9 (1932); *Rubber Chem. Tech.*, **6**, 33 (1933)] has reported cracking of certain unstretched rubber goods upon exposure to sunlight.—C. S. D.

effect of design, or of the combination of several materials in the product, is not made sufficiently clear by an exact knowledge of the properties of the materials (determined on geometrically simple test samples) to permit prediction of whether an article is properly designed or of where the weak places are to be found. It is therefore necessary to test some products in the finished state. Such tests involve both the material and design, and consequently are similar to an equation with two unknowns. (*See* p. 515.)

A decision must be made as to whether a single stress to the breaking point or repeated stressing will correspond (perhaps in an intensified form) to the conditions of service of a product which is being tested in its finished form. An example of the first type is the stressing of railroad brake hose to the breaking point, using water or air pressure. Running an automobile tire on an indoor test machine is an example of the second type of tests. Such machines for testing tires mounted on wheels have been built according to various designs. They have been more or less unsatisfactory in their reproduction of the practical operating conditions of the tires. On the other hand, they have at least the advantage of reproducibility of testing conditions, which in actual practice can never be kept constant.[114]

In the following sections only a few of the most common tests for finished goods will be discussed.

Rubberized Fabric

Adhesion Tests. Adhesion tests might have been considered among the tests run on materials, since a geometrically simple sample is taken and the test shows the mutual effect of two different materials, somewhat as in the abrasion test. Since the adhesion between fabric and rubber is determined on the finished article for the most part, this test is considered at this point.

Since rubber is often used to unite two or more layers of fabric, the determination of the degree of adhesion between the fabric and rubber is a matter of importance. For this test, the upper layer of a sample of uniform width is separated from the lower layer to such an extent that the ends of both layers can be held in clamps, as shown in Figure 194. (The upper layer is often a rubber cover with no fabric.) The determination of the resistance to separation may be made by clamping the sample in a tensile testing machine and noting the load as the tearing is continued. The speed with which the tearing is continued must be held constant because the resistance to further separation (measured in kg. per cm. of width) depends greatly upon this speed. Another method is to measure the speed with which further separation occurs upon application of a certain constant weight.

The thickness of the sample is that of the material tested; width and length are optional within wide limits. The widths most used are 2 to 3 cm. When the force for separation is measured, the length chosen is such as to obtain a sufficiently accurate average value of the force. When the speed of separation is measured, the length selected is that sufficient to give an accurate result for the greatest speed of separation.

The authors prefer the test in which the load necessary to cause further separation is determined, using one or more constant speeds. For such tests the United States Bureau of Standards[115] uses the simple apparatus pictured in

[114] A simple direct test on tire use is performed with so-called electric cars, which use a predetermined amount of electrical energy in passing over a measured distance of level concrete track.

[115] *Bur. Standards, Circ.* **No. 38,** 5th ed., p. 66 (1927).

Figure 195. The force required for separation is automatically recorded. The upper clamp, which is attached to an exchangeable spring (covered by a tube in the illustration), records the elongation of the spring as the ordinate on the drum which is revolved by means of a connection with the driving mechanism of the machine. Any other testing machine of suitable size, equipped with a recording device, may be used for this purpose. If a Schopper machine is used, the ratchet on the load indicator must be disengaged, just as in the hysteresis tests.

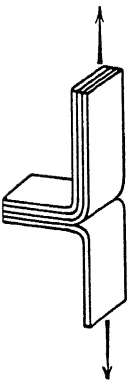


Figure 194—(Left)—Sample for adhesion test.

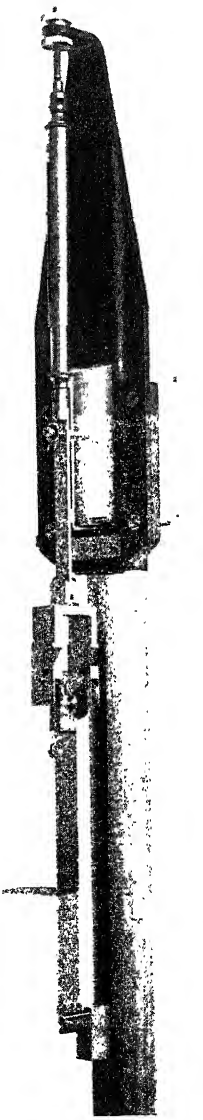


Figure 195—(Right)—Apparatus of the Bureau of Standards for determining adhesion (with automatic device for indicating force).

(Courtesy of Bureau of Standards)

Certain curves obtained by the second method of test (determination of the speed of separation, using different loads) in the Bureau of Standards are reproduced in Figure 196.

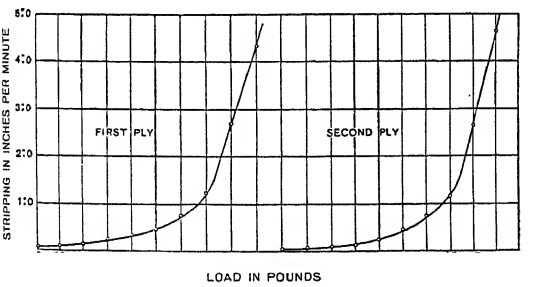


Figure 196—Relation between the speed of separation and the load in adhesion tests. (Bureau of Standards.)

Adhesion tests are run on automobile tires, tubes having fabric reinforcement, balloon fabrics, etc. The method of testing insulating tape given in the specifications of the Verband Deutscher Elektrotechniker embodies the same principles. This latter method (as shown schematically in Fig. 197) deviates a little from that described above. The cylinder has a diameter of 25 mm. The insulating tape which is to be tested for adhesion is previously cut into a length of 500 mm. and is uniformly wound on the cylinder under a tension of 2 kg. per cm. of width.

The minimum allowance for adhesion tests is often simplified by specifying a certain weight which shall cause no further separation.

Figure 197—(Left)—Method of testing the adhesion of insulating tape.

(According to the specifications of the Verband Deutscher Elektrotechniker.)

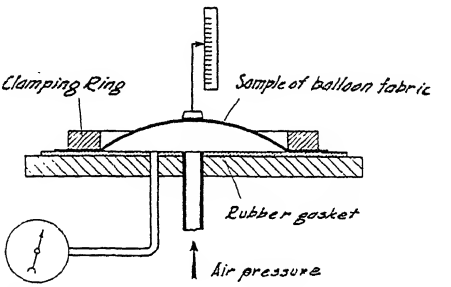


Figure 198—Bursting test for balloon fabrics (or other rubberized cloth).

Testing Balloon Fabrics and Thin Rubber Sheets. The strength of balloon fabrics is determined by tension tests made on strips taken in the direction of the threads of the individual layers of fabric, or by bursting tests conducted on circular samples according to the diagram in Figure 198.

In determining the strength of the fabric from the bursting test, the assumption is made that the circular sample, which has been fastened as in Figure 198, bulges out like a flattened dome. The strength of the fabric S_p is calculated from the formula

$$S_p = \frac{p\,(r^2 + h^2)}{4h}$$

in which

p is the bursting pressure in atmospheres,
r is the radius in cm. of the free portion of the sample,
h is the height of the curvature of the sample at the bursting point.

If an exact flattened dome were actually formed, the calculated strength would be independent of the size of the tested surface of the sample. How-

ever, investigations by Memmler and Schob [116] have shown that the calculated strength decreases somewhat with the increasing diameter of the sample. The authors attribute this to probable local swellings or bulgings which develop more easily in large surfaces than in small ones. Measurements which were made later by Rudeloff,[117] using only one diameter for the samples, showed a regular deviation from the exact spherical form. These results also explain the generally eccentric position of the break in the bursting test.

The determination of the permeability to gases is also very important with balloon fabrics. Although the volumetric determination of permeability requires only a short time, the results satisfactorily indicate the resistance to diffusion of air.

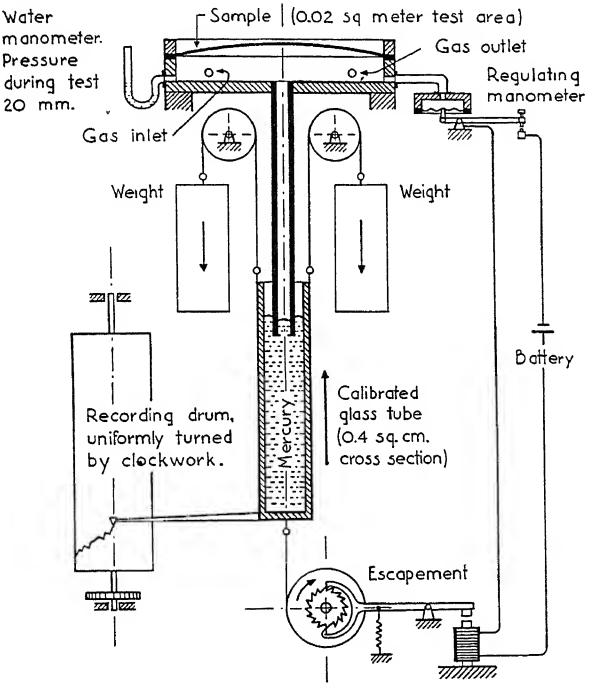


Figure 199—Diagram of Wurtzel's apparatus for the determination of the permeability of balloon fabrics to gases.
(The relay between the regulating manometer and escapement has been left out of the diagram.)

The apparatus of Wurtzel [118] for testing permeability is a suitable instrument which operates on a volumetric principle and gives results in a very short time. A sketch of this apparatus is shown in Figure 199. The hydrogen passing through the circular sample of balloon fabric is measured volumetrically, and the volume is automatically recorded. The sample, which has an area of 200 sq. cm., is fastened at the top of the instrument.

[116] *Mitt. Materialprüfungsamt, Berlin-Dahlem,* **30**, 202 (1912).
[117] *Mitt. Materialprüfungsamt, Berlin-Dahlem,* **38**, 126 (1920).
[118] Manufactured by the firm of Richard Gradenwitz, Berlin.

The space under the sample terminates in a calibrated glass tube open at the bottom. This space is shut off from the outside air by a container filled with mercury. This container is supported by three thin steel bands. These bands are attached to a ring (shown as two individual weights in Fig. 199), which has a greater weight than has the container with the mercury and which consequently more than counterbalances the container, thus causing the latter to be pulled up. It can only rise, however, if the escapement at the bottom (to which it is connected by means of a steel band) is set into operation by the attached electromagnet. The electromagnet of the escapement receives a current through a relay which was omitted from the diagram. A regulating manometer, which is connected with the chamber under the sample, operates the circuit through the relay. The space under the sample is filled with hydrogen at a pressure of 20 mm. of water. The manometer consists of a very sensitive barometric membrane and a contact lever. Should the pressure of the hydrogen fall a little because of the loss of gas through the sample, the electrical circuit is closed and the container filled with mercury is raised an amount corresponding to the volume of gas lost. The original pressure is thereby reëstablished. The upward movement of the container is automatically recorded on the drum, which is uniformly revolved by clock works. Although the test requires 20 minutes, only the middle portion of the graph (covering a period of ten minutes) is used. Since the time required for the test is very short, it is possible to avoid the influence of temperature, which is most troublesome in making volumetric determinations. Errors due to the opposing diffusion of air are also avoided.

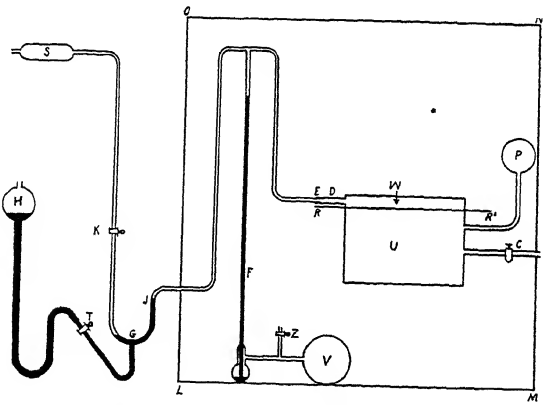


Figure 199a—Apparatus for measuring permeability.
(According to the method of Morris and Street.)

Another apparatus of the volumetric type is that which has been used by Morris and Street [*Ind. Eng. Chem.* **21**, 1215 (1929); also see Morris, *ibid.*, **23**, 837 (1931)] in their recent studies of the permeability of rubber to air.* (*See* p. 513.) Although their permeameter was designed primarily for use with thin rubber sheets or sections cut from automobile inner tubes, it should also be suitable for measurements on balloon fabrics. Their apparatus is shown by diagram in Figure 199a and by photograph in Figure 199b (part outside wooden case does not appear in photograph).

* Translator's note by V. N. M.

The method of measurement with this equipment is essentially a manometric one. Air, under pressure, in one chamber is allowed to permeate into another chamber through the rubber slab being tested. A manometer sealed to the slab allows the change in pressure to be followed. The two air chambers, set in rather heavy iron castings, are indicated by *U* and *W*. A screw clamping arrangement permits the two chambers to be drawn together as tightly as desired on the rubber slab, *RR'*. The latter is also held in position at its ends by clamps (Fig. 199b) whose distance apart is adjustable. It is thus possible to stretch the rubber in one direction to the extent of about 40 per cent. A pressure gage, registering from 0 to 100 pounds per square inch (0 to 7.03 kg. per sq. cm.), is designated by *P*. The brass tube, *D*, from the chamber *B* is sealed with wax at *E* to the glass manometer system, *F*. As the changes in pressure during any experiment are very small, it is possible to use mineral oil as a manometer fluid. The lower

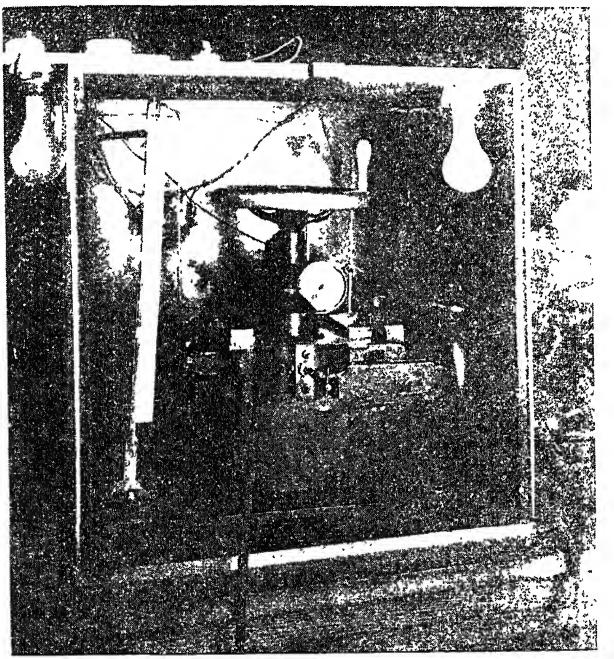


Figure 199b—Assembled apparatus for measuring permeability.
(Firestone permeameter.)

surface of the manometer fluid is not ordinarily open to the air, but is connected to a chamber, *V*, which has a capacity of about 1,000 cc. By means of this system it is possible to adjust the pressure on the manometer fluid at the beginning of an experiment and maintain it practically constant throughout, regardless of the fluctuations of the barometric pressure of the atmosphere. When testing samples of high permeability, however, it is often more desirable to open the stopcock, *Z*, and expose the lower surface of the fluid to barometric pressure. In order to avoid any difficulty from leaking stopcocks, the system is closed by the mercury seal at *G* prior to the beginning of any determination. The drying tube, *S*, contains soda lime. A wooden case, within which it is possible to maintain a fairly constant temperature by means of heating units, a fan, and a suitable thermostatic device, is indicated by *LMNO*. The front of the case is provided with glass windows, arm holes, and rubber sleeves, so that it is possible to manipulate the apparatus without disturbing the temperature control.

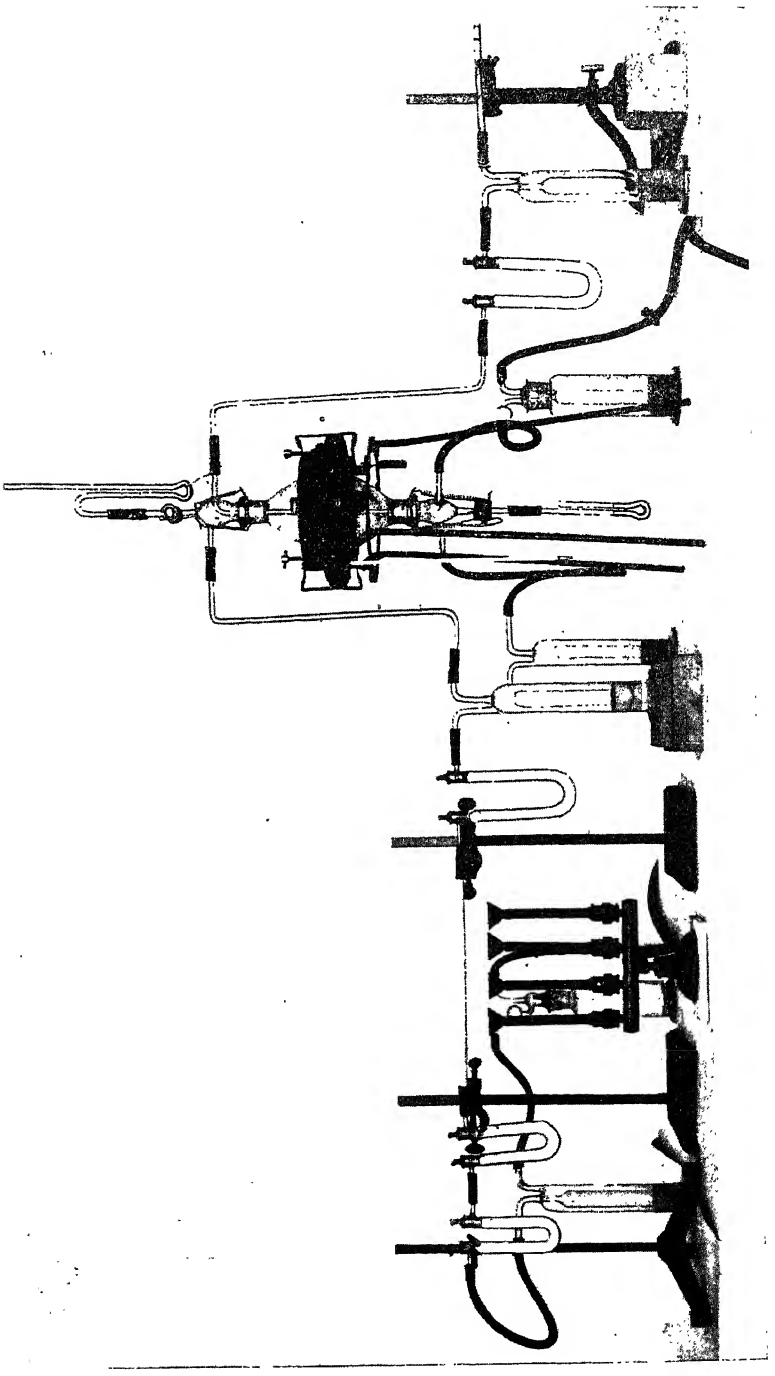


Figure 200—E. Heyn's apparatus for testing permeability.

The method of E. Heyn [119] for the determination of permeability to gases is very accurate, but the manipulation is more difficult. The arrangement of apparatus is shown in Figure 200. The test depends on the burning of hydrogen which diffuses through the sample, using palladium supported on asbestos as the catalyst. The water obtained is then weighed. A disk of the sample is tightly fastened between two funnel-shaped glass vessels. Hydrogen is passed into one vessel and completely dried air is slowly pulled through the funnel-shaped vessel on the other side of the sample. The hydrogen passing through the sample is carried along with the stream of air and is burned to water in a suitable apparatus with the aid of the palladium catalyst. The water is absorbed in absorption tubes and weighed.

The gas interferometer of Haber-Lowe [120] has been successfully used for this purpose. This optical method depends on the differences in the refractive indices of different gases. An interferometer was employed by Edwards and Pickering [121] in their extensive studies on the permeability of balloon fabrics at the United States Bureau of Standards.

A somewhat similar apparatus is that used by Daynes [*Proc. Roy. Soc.* (*London*), **97A**, 273, 286 (1920)] and coworkers in England during the World War.* In their permeameter the actual measurement made is that of the electrical resistance of a platinum wire. This resistance increases with an increase in temperature brought about by the surface combustion of the hydrogen which has passed through the rubber sample.

Railroad Brake Hose and Steam Hose

The Deutsche Reichsbahn-Gesellschaft has prescribed various tests for the inspection of railroad brake and steam hose. A tension test is made on the hose as a whole along the axis. The minimum load which brake hose must withstand is 1,000 kg. For steam hose the requirement is but half as great.

Kinking tests are made on brake hose. Wooden handles are shoved into the ends of the hose to simplify bending the sample. The hose is bent into the shape of a horseshoe until there is a space of 150 mm. between the ends. There shall be no kinking nor shall the resistance to bending be greater than 13 kg.

Another test is that of swinging while internal pressure is applied. The hose is given a to and fro motion of 120 oscillations per minute over a distance of 120 mm. while internal pressure is applied. The arrangement is such that the hose is simultaneously compressed (in the lengthwise direction) 35 mm. at the mean point of its swing, as shown in Figure 201. Brake hose carries a pressure of 7 atmospheres for 10 hours, and steam hose carries a steam pressure of 7 atmospheres for 20 hours, during this test.

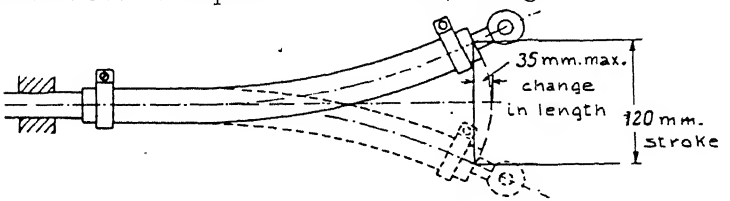


Figure 201—Swinging test with railroad brake hose.

[119] See A. Martens, "The Technical Testing of Rubber and Balloon Fabrics in the Materialprüfungsamt," *Sitzber. preuss. Akad. Wiss.*, **14**, 365 (1911).

[120] See Lunge-Berl, "Chemisch-Technische Untersuchungsmethoden," p. 340, J. Springer, Berlin, **1921**.

[121] *Bur. Standards, Sci. Paper* **No. 387** (1920); *India Rubber J.*, **56**, 753 (1918).

* Translator's note by V. N. M.

Besides these tests, there are also a distension test on the ends, adhesion tests, elongation tests on the lining of the hose, and special tests under conditions of heat and cold.

Rubber-covered Wire

Mention should also be made of certain work which was formerly undertaken at times at the Materialprüfungsamt, which work had as its object the investigation of compounds (high in reclaimed rubber) used for rubber-covered conductors. In a restricted sense, these experiments may be considered as a means of testing soft rubber goods in their marketed form, and therefore they will be briefly mentioned at this place. The work involved torsion tests on samples of rubber-covered wire 2.5 sq. mm. in size and about 50 mm. long. The copper conductor was not removed. Definite conclusions could be formed from the number of twists before tearing started and also from the subsequent formation of fissures on twisted samples which showed no tearing during the twisting.

Several samples illustrating the results of this test are shown in Figure 202.[122]

C. L. Hippensteel [123] describes an apparatus which is used at present by the Bell Telephone Laboratories. This apparatus subjects rubber-covered wire to a compression test to determine the resistance encountered and the deformation which results when an attempt is made to press the conductor through the rubber covering.*

Testing Hard Rubber

Hard rubber is tested much less frequently than soft rubber. This is accounted for by the greater uniformity of its manufacture, its scarcely noticeable aging, and the rather low requirements of strength necessary for most of its uses. Other properties, such as its workability when subjected to turning and drilling, and the ease with which it can be polished, are less easily determined by technical tests. Because of its high insulating properties, hard rubber is extensively used in electrical work, particularly for building instruments. In this use, the probable changes in the resistance of the surface because of oxidation are of the greatest importance.

Testing of Strength

In determining the strength of hard rubber, tension tests are usually not employed, because the material is relatively brittle, and the pressure required to hold the sample may affect the result greatly.† Instead of a tension test, use is made of a bending test, such as is usually carried out on molded materials for the electrical industry.[124] The sample used is a bar, 120x15x10 mm. It

[122] See page 550 with reference to tensile tests on rubber covering which has been removed from the conductor.

[123] *India Rubber World*, **78**, No. 6, 55 (1928); *Gummi-Ztg.*, **42**, 2852 (1928).

* Translator's Note. This machine is manufactured by the Henry L. Scott Co., Providence, R. I. J. H. Ingmanson and A. N. Gray [*India Rubber World*, **82**, No. 4, 53 (1930)], have used it in working out a method for evaluating rubber-covered wire by correlating compression, shear, and adhesion tests with bomb aging. — V. N. M.

† Translator's Note. An extensometer, which enables the small elongations and hence the stress-strain properties of hard rubber to be measured on the Scott tensile-testing machine, has recently been described by B. L. Davies [*Trans. Inst. Rubber Ind.*, **9**, 130 (1933)]. Satisfactory stress-strain curves with specimens exhibiting an ultimate elongation of less than 3 per cent are readily obtainable by means of this device. These curves were found to provide a reliable means whereby stocks containing different accelerators and other compounding ingredients may be compared. The results obtained indicate that ebonite exhibits plastic flow and thus does not deform exactly in accordance with Hooke's Law. — V. N. M.

[124] See "Vorschriften des Verbandes Deutscher Elektrotechniker, V. D. E."—Drucksache No. 318, 318a.

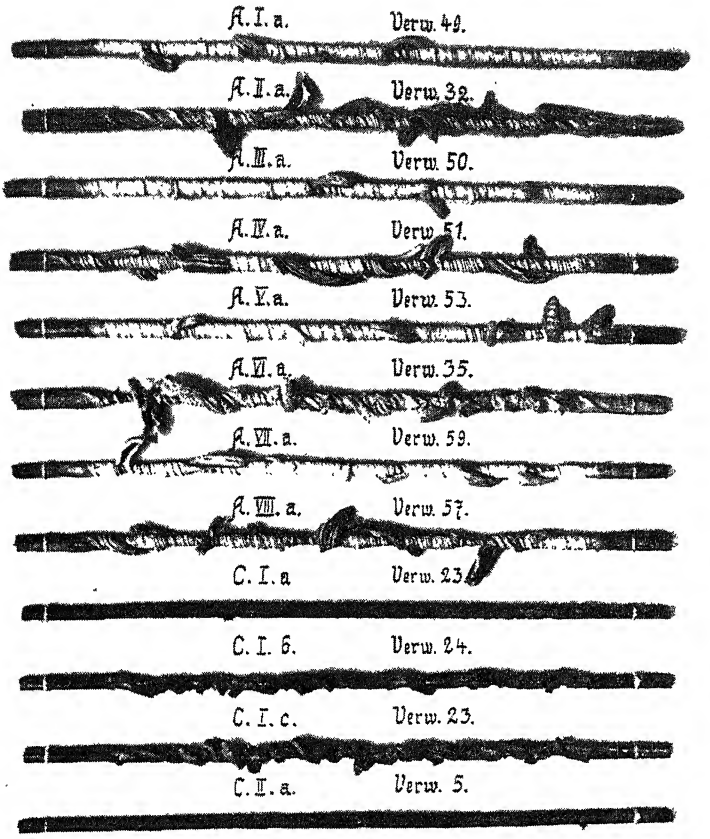


Figure 202—Twisting tests with rubber covered wire. (The number following "Verw." is the number of twists necessary to cause the first tears to appear in a sample 100 mm. in length. The photographs were taken 24 hours after twisting.)

is placed on supports 100 mm. apart and is subjected to stress by means of a cylindrically shaped element having a radius of 10 mm. (*See* Fig. 203.) In the simplest procedure, the load at break and the amount of bending are determined. If the material shows a large degree of bending, the load causing a certain bending (for example, 5 or 10 mm.) is determined. Should more complete information concerning the properties of the material be desired, the entire course of the loading and bending may be automatically recorded by the machine.

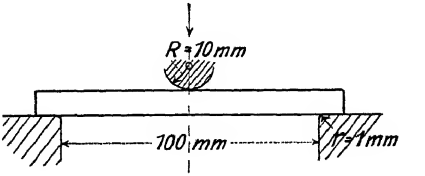


Figure 203—Bending test for hard rubber, using standard bars.

Samples of the same dimensions (standard bars 120x15x10 mm.) are used to test the resistance of hard rubber against bending stresses caused by blows. The apparatus which has been used for this purpose employs a pendulum for striking the blow. This apparatus is similar to the Charpy pendulum hammer which is used in various sizes for testing metals. The apparatus, which is made by L. Schopper of Leipzig, is provided with two exchangeable pendulums having impact energies of 10 and 40 kg. cm. respectively. (*See* Fig. 204.) The supports for the sample are cut back at an angle of 15° and have the corners where the bending occurs rounded to a radius of 3 mm. The distance between these supports is 70 mm.

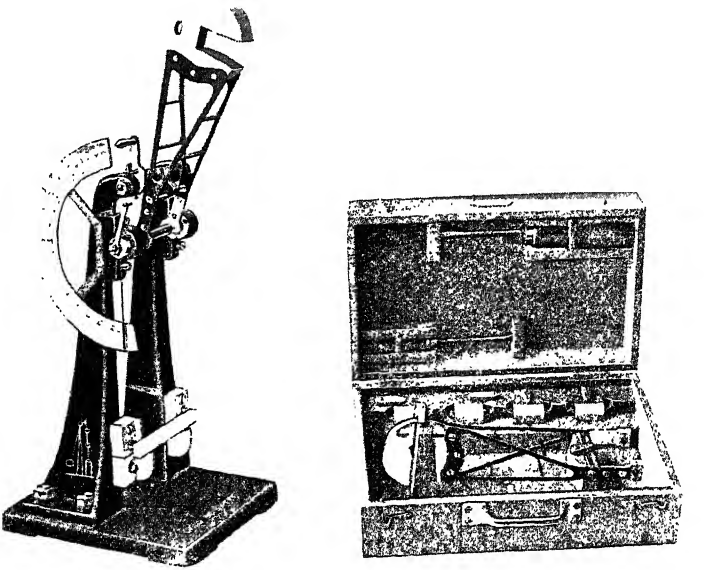


Figure 204—Pendulum hammer with exchangeable pendulums having impact energies of 10 and of 40 kg. cm. (L. Schopper).

Compression tests are sometimes made on hard rubber. For this test a cylindrical shape for the test sample is preferable to a square one, because the preparation of the former is easier and cheaper. To avoid the effect of flaws, the height of the cylinder must not be more than 2½ times the diameter. For the standard form of a cylinder made for compression tests, the height equals the diameter.

Occasionally, torsion tests are also performed on hard rubber.

The Brinell test is used to determine the hardness of hard rubber. As a rule the 5-mm. steel ball is used, with a load of 50 kg. Hard rubber resembles soft rubber in that an appreciable portion of the penetration of the ball is due to elastic deformation. The total depth of penetration, therefore, is measured while the load is being applied. Since there is likely to be an "after-effect," readings are also made 10 and 60 seconds after the load has been applied.

The degree of hardness H, expressed as kg. per sq. cm., is calculated by the formula

$$H = \frac{P}{\pi h D} \quad \frac{C}{h}$$

in which P is the load applied to the ball in kg., h is the penetration in cm., and D is the diameter of the ball in cm. If P and D are the same for several tests $\frac{P}{\pi D}$ may be combined as the constant C. For $P = 50$ kg. and $D = 0.5$ cm., C is 31.8.

In several applications, hard rubber is attached to soft rubber or to metal by vulcanization. A satisfactory adhesion to these other materials must be developed. Adhesion to both soft rubber and iron is required in the same article in the case of solid tires for automobiles, trucks, etc.

In testing, a hack saw is used to cut a slab 1 cm. thick from the solid tire or from a section vulcanized solely for test purposes. One or more samples are made from this slab, as shown in Fig. 205. A hole is bored through the iron portion, and the sample is fastened to the upper grip of a tensile machine by a pin. The broadened end of the soft rubber part of the sample is clamped in the lower grip of the machine. Great care must be exercised in the preparation of the sample to prevent damaging it. The load must be applied without a jolt and must continue with uniform speed.

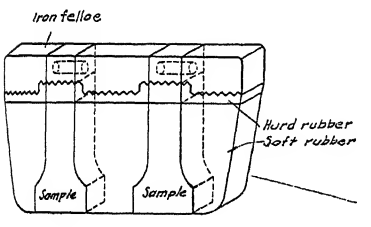


Figure 205—Method of obtaining samples for adhesion tests on solid tires.

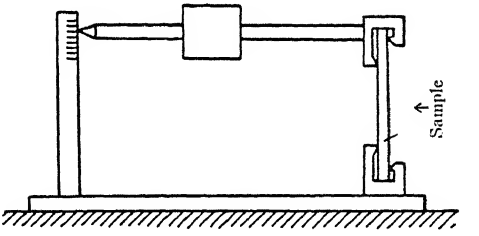


Figure 206—Diagram of the Martens' test for the determination of resistance to heat.

Heat Tests

Insulating materials for the electrical industry are occasionally used at temperatures above room temperature, and must be able to resist deformation under such conditions. The specifications of the Verband Deutscher Elektrotechniker include special tests for the resistance to deformation at higher temperatures; namely, a bending test (the so-called Martens' test) and a penetration test.

Martens' Test. The test bar for the Martens' test is held in a vertical position (Fig. 206) and is subjected by means of a weighted lever to a uniform bending stress of 50 kg./sq. cm. The temperature of the sample is raised 50° C. per hour in an oven. A pointer on the end of the lever 240 mm. from the center of the bar shows the declination of the lever on a millimeter scale. The temperature at which the end of the lever (240 mm. long) falls 6 mm. is called the "Martens' number." Should the bar break before the declination of 6 mm. is reached (this does not occur with hard rubber), the

temperature at which the break occurs is the "Martens' number." Although the temperature of the air near the sample is 5 to 6° C. higher than that of the interior of the bar, the former is used for this determination.

Since a relatively large number of samples is simultaneously heated in an oven in the usual test, it is desirable to make use of electrically-operated signalling devices. Contacts are attached to the ends of the weighted levers. When a lever falls to the 6 mm. limit the contacts close the electrical circuit of a lamp or bell. The contacts must be kept very clean to avoid faulty

The Martens' test is not severe, because the Martens' numbers are for the most part considerably under those temperatures at which the finished articles may be used without damage. The difference between the Martens' number and the maximum temperature of safe use is especially great with hard rubber. The Martens' test does not show sufficient differences between different hard rubber compounds.

Needle Penetration Test. The so-called Vicat needle was introduced as a test for insulating materials because the hard rubber industry found such a test necessary. The manner of conducting the test deviates considerably from the original Vicat test of the standard cement tests. The needle carries a much heavier load; namely, 5 kg. (11.02 lbs.), corresponding to 500 kg. per sq. cm. (7,110 lbs. per sq. in.). Moreover, the measurement of the penetration must be done with greater precision. Figure 207 shows the

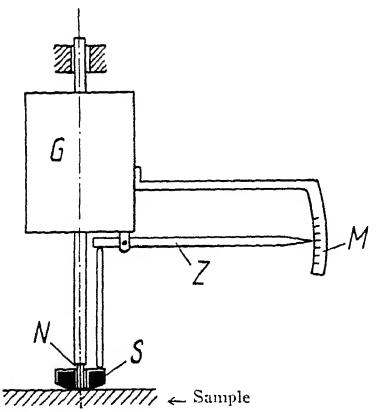


Figure 207—The needle penetration test. (Vicat needle.)

principle of the apparatus, which was designed by A. Schob. The needle N of 1.13 mm. diameter (1 sq. mm. in cross section) is ground flat. A 5 kg. weight G furnishes the load on the needle. The slightly rounded piece S rests on the surface of the sample. The relative motion of the needle N with respect to the piece S is multiplied by the pointer Z and is indicated on the scale M. The temperature at which the needle is pressed into the sample to a depth of 1 mm. is the "Vicat" value. The system of raising the temperature is the same as in the Martens' test.[125]

[5] A more complete picture of the changes in properties with changes in temperature is obtained by conducting the bending tests (as described on p. 629) at different temperatures.

Test for Resistance to Fire

The materials used for insulation in electrical installations must often be more or less resistant to fire. Hard rubber is an easily ignited substance, but its combustibility can be somewhat reduced by suitable compounding. Methods for the determination of the resistance of insulating materials to fire were first partially developed by the Verband Deutscher Elektrotechniker. The early method, which involved the use of a Bunsen burner, has been abandoned. The resistance to high temperatures has been divided into resistance to glowing heat and resistance to flame. Methods for the latter are still being developed. The specifications for the determination of the resistance to glowing heat (as published in the Elektrotechnische Zeitschrift)[126] are shown below.

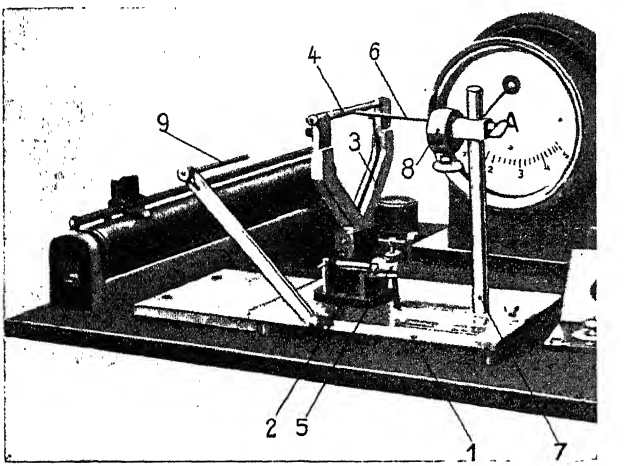


Figure 208—Schramm's apparatus for determining the resistance of insulating material to glowing heat.

"Samples for the test are to be of the following dimensions: thickness $a = 3$ mm.; width $b = 15$ mm.; length $L = 120$ mm. Samples which are shorter than 120 mm. may be used if the combustibility is low. These can be made by grinding down the standard bar. The method of test may also be applied to material obtainable in thicknesses less than 3 mm. The tests are to be performed in triplicate.

"The resistance to glowing heat is to be determined by the apparatus designed for that purpose by Schramm. (*See* Fig. 208.) A block (2), which can be revolved, is fastened to a base plate (1). The block carries a movable, insulated holder (3) on which rests a rod of silicon carbide (4). This rod, which is 8 mm. in diameter and which has a free length of 80 mm., is heated electrically. The apparatus can be operated at 110 volts or higher voltage with direct or alternating current by using suitable regulating resistances. During operation the apparatus must be protected from air currents. The counterbalancing weight (5), which has an adjusting screw, serves to limit the movement of the silicon carbide rod to 5 mm. as it follows the burning of the sample. A movable support (7) and the clamp (8) hold the sample (6) in place. A rod (9), which can be swung into place instead of the silicon carbide rod, is used to adjust the sample.

[126] *Elektrotech. Z.*, [49], **29**, 1094 (1928).

"The test bar is weighed to an accuracy of 10 mg., is then fastened in the clamp, and is finally adjusted at the middle of the rod (9) which has been swung up into the position finally to be taken by the silicon carbide rod. The sample is so adjusted that its edge (that edge which is 15 mm. long) will rest against the center of the silicon carbide rod. The rod is heated while in the lowered position to 950° C. This temperature is reached by adjusting the current (as shown by an ammeter) to the required value given in the standard curve accompanying the apparatus. With a potential drop of 100 volts across the silicon carbide rod, a current of approximately 4 amperes is required. The temperature becomes constant when the pointer of the ammeter becomes stationary. As soon as this occurs, the rod used in adjusting the sample is swung down and the heated rod is swung into place. After three minutes, the flame if present is extinguished. Should the material be very combustible the flame is extinguished at the instant it reaches the clamp holding the sample. The sample is removed and the loss in weight is determined in milligrams. The extent of the burning is measured in centimeters. In rounding off the figures for the extent of the burning, values under 1 cm. are raised to 1 cm.[127] Values above 1 cm. are reported as the nearest whole number of centimeters.

"If, because of the high combustibility of the material, the test has been stopped before the end of the three-minute period, the loss in weight and also the extent of the burning are calculated to three minutes. Both of these values are assumed to be directly proportional to the time.

"The product of the two values determined, i.e. the loss in weight in milligrams and the extent of burning in centimeters, expresses the degree of fire resistance. The arbitrary basis for rating is as follows:

Product (mg. x cm.)	Degree of resistance to fire
Over 100,000	0
100,000 to 10,000	1
10,000 to 1,000	2
1,000 to 100	3
100 to 10	4
Under 10	5

The value 0 indicates very combustible materials; the value 5 is for incombustible matter."

Electrical Tests

Since hard rubber is one of the best electrical insulators, it is scarcely necessary to test the electrical properties of pure hard rubber. However, since hard rubber compounds differ in quality and composition, the testing of the electrical properties can be a matter of importance

For most purposes, the determination of the resistance to leakage on the surface is sufficient. The method described in the publications of the Verband Deutscher Elektrotechnischer is as follows:

"The resistance to surface leakage is measured over a surface area 10 cm. long by 1 cm. wide at 1,000 volts D.C.:

(α) as received, but after grinding the surface;

(β) after immersion in water for 24 hours;

(γ) after immersion in a 25 per cent solution of sulfuric acid for three weeks;

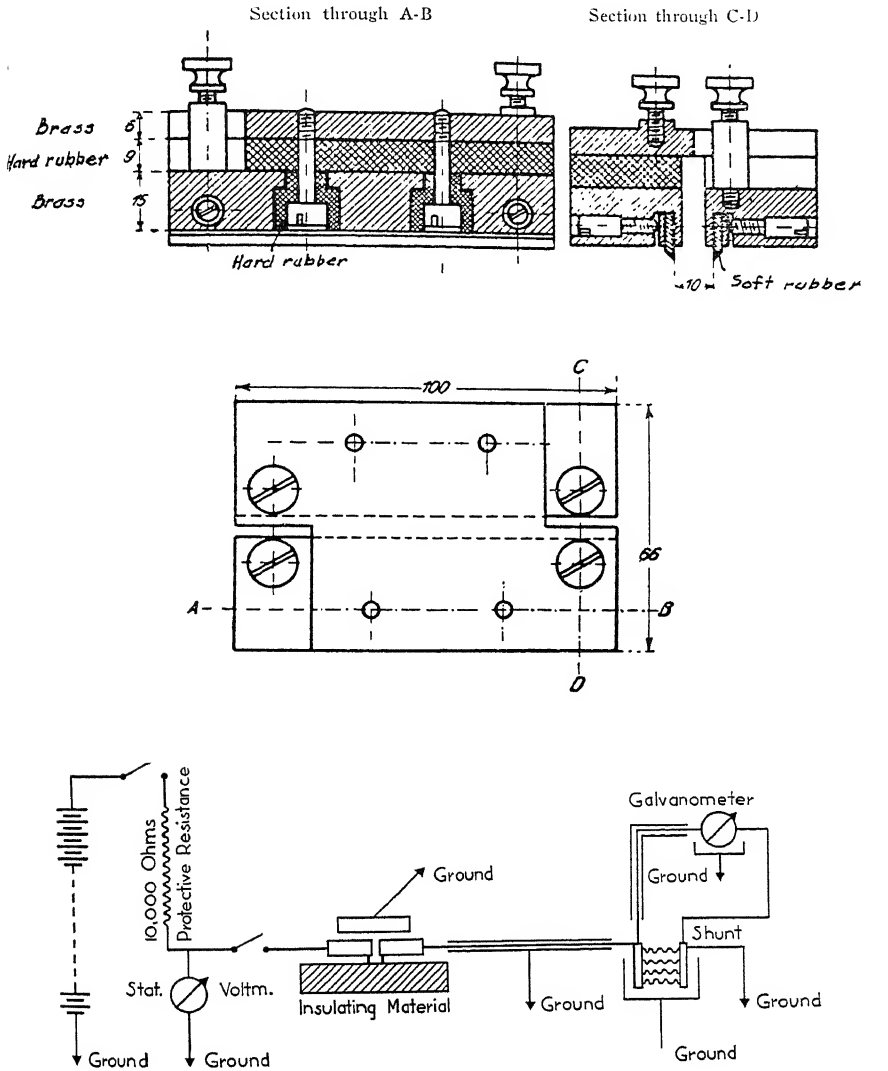
(δ) after three weeks' exposure to ammonia fumes.

"In tests (β) to (δ), the change in weight is determined and expressed in per cent.

"To measure the resistance to leakage of a surface, two electrodes made of rubber and tinfoil, 10 cm. long and 1 cm. apart, are placed on the sample. (Refer to the standard apparatus in Figs. 209 and 210. Figure 211 shows the diagram of the circuit.) One electrode is connected through a protecting resistance of 10,000 ohms to the negative side of a 1,000-volt direct current circuit, the positive side of which is grounded. In the circuit used in the measurement, one electrode is connected to one terminal of the galvanometer shunt; the other terminal is grounded. To exclude stray currents, the lead to the shunt and from there to the galvanometer must be protected by a grounded case. The plate holding the electrodes is grounded, as is also the support for the galvanometer and shunt. The sensitivity of the galvanometer should be at least 1 x 10^{-9} amperes for a 1 mm. division with the scale 1 meter from the galvanometer. With the aid of the shunt, it is possible to set the sensitivity at 1/10, 1/100, 1/1,000, 1/10,000 and 1/100,000 of the maxi-

[127] This has since been changed. Values under 1 cm. are reported to the nearest millimeter.

mum value. A switch on the shunt serves to short-circuit the galvanometer. To calibrate the galvanometer reading, the 1/10,000 shunt is used with a wire resistance of one megohm instead of the 'surface leakage' resistance apparatus. The standard megohm, which is wound unifilar with manganin wire 0.05 mm. in diameter, need only be accurate to 3 per cent. The protective resistance consists of 0.1 mm. manganin wire wound unifilar on a porcelain or glass tube about 6 cm. in diameter and 50 cm. long. An accuracy of 3 per cent is sufficient for this resistance also. A static voltmeter measures the voltage between the low side of the protective resistance and the ground.



Figures 209-211—Standard apparatus for determining surface leakage resistance (V.D.E.).

"**Experimental Procedure.** With the switch between the protective resistance and the 'surface leakage' apparatus open, the direct current is set at 1,000 volts, using the static voltmeter. The galvanometer is then short-circuited, and the switch to the 'surface leakage' resistance apparatus is closed. Should the voltage drop below 500 volts, the resistance to leakage on the surface of the insulating material is less than 10,000 ohms. Should the voltage remain above 800 volts, it is possible to use the galvanometer for the measurement.

"The galvanometer is read one minute after the voltage is applied.

"The scale used for comparison is as follows:

Resistance to Leakage at the Surface	Comparison Number
Under 1/100 Megohm	0
1 to 1/100 Megohm	1
100 to 1 Megohms	2
10,000 to 100 Megohms	3
1 million to 10,000 Megohms	4
Over 1 million Megohms	5

"For each series of tests, three slabs[128] are prepared, and at least two determinations are made on each. The slabs used for test β may also be used for test γ.

"*Test* β. After the slabs are taken out of the water, they are wiped off with a cloth. They are then allowed to remain vertical for two hours at room temperature in still air to remove the adhering moisture from the surface. Then the determination may be made.

"*Test* γ. The slabs are removed from the sulfuric acid solution and washed about one minute in running water. The determination is then finished as under β.

"*Test* δ. The slabs are suspended in large glass containers, on the bottom of which a small volume of saturated solution of ammonia is placed. The containers are covered with glass plates. Ammonia is added every two to three days to make up for the losses resulting from vaporization. After removing the slabs from the containers and examining them, they are wiped with a dry cloth and measured."

Of course, other electrical tests, such as dielectric strength, dielectric loss, etc., are made in certain cases. These tests can only be mentioned here. For detailed descriptions of them the reader must go to the special technical literature.[129]

[128] To simplify the testing of hard rubber, the standard pieces (120x15x10 mm.) have recently been used for measuring surface leakage resistance.

[129] H. Schering, "Die Isolierstoffe der Electrotechnik," J. Springer, Berlin, 1924.

Microscopy of Technical Vulcanizates

By H. Pohle*

History. General Assumptions

The earliest microscopic discoveries in the field of technical vulcanizates were probably made by P. Breuil,[1] who is therefore to be considered as the originator of this branch of applied microscopy. The method first attempted, which involved the application of metallographic methods, did not prove very successful. The later investigation of thin sections by transmitted light, also first tried by Breuil, was much more successful, and led to the accumulation of colloid chemical information of interest in connection with the modern field of vulcanized rubber products. Although Ditmar[2] made some contributions to the technique of thin sections, much of the important work of recent years in the field of microscopy has been carried out by American and English investigators. Depew and Ruby,[3] and also Green,[4] made use of the microtome and of histological methods of preparing specimens, such as freezing and hardening the object. Finally Ames,[5] in extending the work of Depew and Ruby, further developed the apparatus for the preparation of frozen sections, and at the same time reported new discoveries.†

With the exception of the scientific work of the past few years, the introduction of microscopic methods into the rubber industry has not been as rapid as might have been expected, nor has it taken the place in rubber testing that its importance demands. The reason for this should not be misunderstood. The cause lies not so much with the technique of preparing specimens, as with the difficulty of obtaining that clear conception of the variety of microscopic phenomena which is necessary for the proper interpretation of facts. The many kinds of information that can be obtained by microscopic methods should not be underestimated, and should be given consideration in connection with the economic and technical specifications of materials for the rubber industry.

Almost all compounding ingredients exist today in several commonly used varieties, which might without examination be mutually substituted, but which show noticeable differences on technical testing. It is not always possible to detect chemical differences between two brands of the same product, but it is often quite easy by microscopic examination to establish differences in the degree of subdivision of the two brands, thus providing a physical or "morphological" explanation for observed variations in behavior. The establishment of such relationships has been the occasion for making whole series of dispersion studies on the different commercial brands of compound-

*Translated by H. P. Coats.

[1] *Compt. rend.*, **140**, 1142 (1905); and *Caoutchouc & gutta-percha*, **2**, 82, 118, 158, 197 (1905).

[2] Ditmar, R., "Analyse des Kautschuks," Hartleben, Leipzig and Vienna, **1909.**

[3] *Ind. Eng. Chem.*, **12**, 1156 (1920).

[4] *Ibid.*, **13**, 1130 (1921).

[5] *J. Roy. Microscop. Soc.*, p. 265 (1923).

† Translator's Note. See also Grenquist, E. A., *Ind. Eng. Chem.*, **20**, 1071 (1928); **21**, 665 (1929), and Steele, T. F., *Ind. Eng. Chem., Anal. Ed.*, **2**, 421 (1930).—V. N. M.

ing ingredients (pigments) which are of a type suitable for microscopic analysis.[6] The knowledge gained thereby has also made it evident that the problem of microscopic analysis has taken on primarily a "quantitative" aspect with respect to the degree of subdivision of the pigments, since this property permits conclusions to be drawn not only regarding the origin of the pigments but also regarding the properties of the vulcanized product.

An evaluation of microscopic information from the point of view of dispersoid analysis is based upon the assumption that this information shows rubber to play the role of a dispersion medium. It is found that the characteristic degree of dispersion of a pigment is being approached during mixing, and has usually been attained, at the latest, by the time the original mixing and the subsequent "warm-up" have been completed. An appreciably longer period of working does not produce a misleading alteration of the microscopic picture. Once this state of dispersion is reached, it remains surprisingly stable and permanent, even during the vulcanization process. This observation applies even down to a state of "colloidal dispersion" (compare discussion in connection with transmitted light, p. 647) and explains the fact that finished products of widely different sources and treatment (kneaded, milled, cold-cured, hot-cured) all show a similar degree of dispersion; i.e., that which is typical of the pigment concerned.

On the other hand, it is not to be expected that pigment particles of the same size (as measured microscopically) will lead in every case to the same results as determined by the physical testing of the finished rubber product, since here, as in all technical products, one must reckon with coarse structural disturbances which cannot always be discovered in a microscopic field. For instance, when small thin sections are examined by transmitted light, the various inhomogeneities disappear. With reflected light, on the other hand, at least a part of them can be observed. In avoiding such disturbances, it is not only a question of preventing large inclusions by the exclusion of air and the like, but also preventing fine cracks or strains which may act as the starting point of larger fractures. Such structural inhomogeneities frequently lie deeply imbedded in the rubber and can only be detected by special adaptations of the methods of preparation. As long as it is impossible to avoid such inhomogeneities of microscopic dimensions, it is necessary to reckon with the consequent phenomena and to interpret the results of measurements of tensile strength and elongation with this in mind. On the same grounds, it is unsafe to attempt any interpretation of the results of physical testing on the basis of theoretical considerations regarding the molecular structure of rubber.

The following compilation of microscopical data has been obtained from the practical experience of the past ten years, and covers the microscopy of technical vulcanizates as completely as this experience permits. The complementing of chemical analysis, and in many cases the replacement of the same by the quicker microscopic examination, as well as the control of manufacturing processes by following the changes which occur during the fabrication, have constituted the major interests during these years. The division of the material to be discussed in this section has not been made upon this basis, however, but rather according to the method of investigation used. At the same time the attempt has been made to classify the pigments on the very practical and important basis of the degree of the subdivision, since in

[6] By performing a series of experiments, it is possible to establish that differences are not accidental ones resulting from a lack of reproducibility, but are rather to be explained on the basis of characteristic effects of the raw materials themselves.

this manner it is possible to indicate most clearly to what extent our present knowledge in the field of rubber pigments and rubber compounding needs to be enlarged. The results to be presented indicate that a definite contribution to colloid chemistry has been made by the study of the various pigments, and form perhaps the foundation of a new chapter in colloid chemistry on the subject of "Dispersion in Rubber." Furthermore, these results are of great scientific interest, since they have been obtained with dispersions in which the concentration of the dispersed phase can vary over unusually wide limits, and with which the most important physical properties can be controlled by proved testing methods.

The writer is very grateful for the many autochrome photographs which were placed at his disposal by the Continental Caoutchouc and Gutta Percha Company of Hanover.

Preparative and Optical Aids

The equipment ordinarily used in fine histological work is also applicable to the examination of thin sections by transmitted light. With a few simple additions, it can be made to serve as well for the ordinary observations by reflected light or in the dark field.

Preparation needles ("teasers"), scissors, and knife (razor blade) should be of fairly strong material, because considerable resistance is encountered in the separation or cutting of material from solid tires or pneumatic tires. A very useful tool in the preparation of thin sections by hand is the double knife of Schieferdecker or the similar and smaller tool of Orth. In the latter the blades must be set exactly parallel. Ditmar has recommended that thin sections be made more transparent by re-pressing them between slide and cover glass. If success is to be attained with thin sections of cured stock rich in fillers, a stout apparatus is required. A suitable arrangement, which has been widely used, consists of two pieces of plate glass, 60x45x6 or 7 mm., which are held or pressed together by means of a pair of screws (method of R. Goetze of Leipzig). Space is provided between the screws for the average slide as well as for the usual movements of the objective. The thickness of the glass plates necessarily limits the magnification to a small value. A specially corrected objective is preferred (for example, the Leitz T3 objective, with a magnification of about 13×).

In preparing a specimen for investigation by reflected light, use is made of a grinding wheel, such as those often to be found on abrasion machines. Since most vulcanized materials tend to smear on application of finer polishing paper, the whole process of polishing is carried out with the same coarse-grained abrasive, the desired smoothness being obtained by varying the pressure and speed.

For the grinding and fine polishing of hardened samples of rubber,* F. H. Roninger [*Ind. Eng. Chem., Anal. Ed.*, **5**, 251 (1933)] found that an automatic polishing machine of the type designed by S. Epstein and J. P. Buckley [*Bur. Standards J. Research*, **3**, 783 (1929)] gave satisfactory results.

Since the various pigments differ considerably in particle size, it is necessary to include at least 3 objectives in the optical equipment. Clear images and colors without details are shown best by an achromat of about 10× magnification, such as the above-mentioned objective T3. The smaller particles of pulverized minerals, factice, etc., are brought out quite clearly by a

* Translator's note by V. N. M.

medium objective of 40× magnification. Particles of the type represented by gas black and zinc oxide, which are frequently submicroscopic in size, are best seen by using an oil immersion objective with a numerical aperture between 1.3 and 1.4. Depew and Ruby referred to this fact. For subjective observations, apochromatic lenses are generally unnecessary, since the less costly fluorite objective serves the same purpose. Particles giving a brownish-red dispersion color are most sharply contrasted in a blue light.[7] A very obvious supplement to the oil immersion objective is an efficient source of light (preferably with a condenser of numerical aperture 1.4) to utilize completely the large aperture of the oil immersion objective.

In the case of examination by reflected light, a very useful supplement to the optical equipment is an objective of 5× magnification for use in low-power work. With the two lowest-powered objectives it is possible to carry on investigations with oblique reflected light. A small concave mirror above the microscope makes possible oblique illumination from any desired direction, as well as the projection of ultra-violet light. A reflector which can be fitted to the head of the objective facilitates the production of a concentrated and intense beam at a very small angle (for reflected light). Since this reflector receives its light from the lower mirror of the lighting source, an opening about 50 mm. wide is provided in the center of the stage. It is obvious that large specimens, which do not allow a free passage of light, cannot be very satisfactorily illuminated. Observations at higher magnifications (such as are never attained during experiments with transmitted light) are possible only with vertical reflected light from a vertical illuminator of the usual construction; and also require a special, short-mount objective. As will be shown below, the vertical illuminator is used with oil immersion objectives of various magnifications, and recently also with low-powered objectives, such as the 16 and 8 mm. focal length objectives of E. Leitz. With these last mentioned objectives, the rubber surfaces are directly under the immersion oil and are examined without the use of cover glasses.

Changing over to dark field examination necessitates a small iris diaphragm, which is inserted between the head of the objective and the microscope tube (Leitz), or which is supplied with the special objective to which it is fixed (Zeiss). The image obtained in a dark field depends upon the proper position of this diaphragm. The illumination of the specimen is accomplished by means of the usual dark field condenser, after removal of the ordinary condenser. The ultra-condenser must be focused in the center of the field and on the preparation. For microscopes which do not have a centering device on the tube or illumination apparatus, there is a new form of condenser (designated by Leitz as a plate condenser), which is so flat that it can be laid upon the stage. The centering of the focal point in the field is accomplished by sliding the plate, while the vertical position is adjusted by means of a lever. A so-called luminous spot-ring condenser, constructed by Zeiss, can be used with the highest oil immersion objective of 1.3 numerical aperture, practically no screening by means of the iris diaphragm being necessary. With this arrangement, most of the high resolving power of these objectives is made available for dark field observations. These highly valuable optical tools are applicable to even the smallest preparations.

As a light source, it is desirable to have a self-regulated arc lamp with a converging lens. The substitution of a quartz lens for the glass lens, and the

[7] Lifa filter No. 1658/26 (Daylight filter).

insertion of an ultra-violet "black" glass filter,* provides a source of ultra-violet light suitable for most work. The complete removal of red radiation from such light by passing it through a 3 cm. layer of a 10 per cent solution of copper sulfate is not always desirable, since the non-luminous particles become entirely invisible in such a case. Sometimes the mercury lamp is used in combination with the same "black" glass (Heräus ultra-violet analyzing filter). Magnification of poorly lighted specimens is obtained only with the two lowest-powered objectives. By the insertion of a 15 mm. central stop in the ordinary illuminating apparatus, use may also be made of the simple dark field for low magnifications. (*See* "Investigations in the dark field"; p. 670.)

Mention† should be made of certain equipment which has recently been developed, and which has been used particularly during microscopic studies of vulcanization. An example of this is Dannenberg's [*Kautschuk*, **2**, 276 (1926)] "squeezing-chamber," which facilitates the observation with the microscope of samples before and after vulcanization. Grenquist [*Ind. Eng. Chem.*, **20**, 1073 (1928)] used this device in his preliminary microscopic studies of vulcanization. "Squeezing-chambers" provided with means for controlled heating have made possible the microscopic observation of the entire process of vulcanization. [*See* Dannerberg, *Kautschuk*, **3**, 104, 128 (1927) and Grenquist, *Ind. Eng. Chem.*, **21**, 665 (1929).] Dannenberg's electrically heated device has been improved by Walton [*Ind. Eng. Chem., Anal. Ed.*, **1**, 106 (1929)], who utilized a thermocouple to permit accurate temperature control. Hauser, Miedel, and Hünemörder [*India Rubber World*, **79**, No. 1, 59 (1928); *Colloid Symposium Monograph*, **VI**, 207 (1928)] have also described a microscopical attachment to effect vulcanization under the microscope, using steam as the heating medium.

Investigations by Reflected Light

Observation by reflected light is the best method for preliminary investigation, because of the simplicity of the preparation of the specimens. As a rule this method also furnishes the best criteria as to whether later examination by transmitted light might bring results, and whether thin sections should be used. In establishing the identity of and examining the dispersion of the individual components of a mixture, examination by reflected light cannot usually displace the bright field investigation, because the intensity of light by the former arrangement is limited and furthermore good images do not result when large magnification is attempted (as in the case of measuring the finer pigments). An attempt to use a procedure similar to that employed in metallographic studies does not give the desired results, since the preparations thus made available are not suitable for vertical illumination, either optically or with respect to surface structure.‡

The advantage of examination by reflected light lies in the fact that it frees the investigator from the troubles which are encountered during the preparation of sections with very small dimensions and makes possible the examination of larger objects by utilizing fields of larger diameter and thus obtaining a more general view of the surface. It is possible to obtain information concerning the physical structure of such vulcanizates as are built up of individual layers and concerning the nature and distribution of material appearing on the surface as "bloom." The irregularities resulting from working and vulcanizing also become evident, often only as vaguely bounded colorings, which can be recognized only in the larger, smoother, more uni-

* Translator's Note. Similar filters, such as red-purple Corex A, are made in America. Three such filters, obtained from manufacturers in different countries, were recently compared by V. N. Morris [*Ind. Eng. Chem.*, **26**, 107 (1934)]. Also *see* page 642.

† Translator's note by V. N. M.

‡ For a discussion of recent work along this line, *see* p. 646.

formly lighted surfaces which can be observed by reflected light. The method is also useful when the point in question is one of testing the degree of technical homogeneity of larger objects; for instance, with respect to air holes and separations which are rarely to be found in a thin section. Furthermore, the method is of service for determining a whole series of characteristic structural phenomena ("reinforced" structures, "calender" structures)* which up to this time have been neglected in microscopic investigations, but for which the magnifying power of an ordinary reading glass is not sufficient. Although such structures usually occur in connection with very fine dispersion of pigments, they are also to be observed to some extent in the broader pictures obtainable with microscopes of lower power.

The determination of the structural forms in larger preparations makes it possible to recognize the direction of layers and laminations (grain) and to determine the processing method (for example, tubing or calendering) which has been used.[8] It also discloses certain stress phenomena which seem to lie within the rubber substance itself and which cannot be ascertained by observation with transmitted light, since the usual method of preparation of thin sections does not permit any picture of the rubber substance to be obtained (Plate II, Fig. 3). The consequences of such phenomena are of interest in connection with the results of physical testing, because occasionally they provide an explanation of the variation in results with the direction of testing.

As the following examples of applications show, convenience is the consideration which governs the choice of the particular method to be used when the surface of a specimen is to be examined. The examination under low magnification permits the objective to be some distance from the object and enables the use of oblique reflected illumination.

If blooming is to be studied first, it is of advantage to allow the blooming to occur on a surface that has been cleaned with ether (in order to obtain characteristic crystals). A further differentiation of the image is obtained by the use of oblique reflected ultra-violet light, since substances which bloom are usually capable of luminescence (anthracene, accelerators, sulfur, selenium and antioxidants—but not oxidation products of the latter). The light from a mercury or carbon arc is passed through a filter and then projected on the preparation by a small concave mirror. The luminescence, which occurs at the point of focus, may serve as a means of identification of the material being examined. The extension of the observations of luminescence to the non-blooming portions of the compounded stock is made difficult because of the interfering luminescence of the vulcanized rubber substance itself. (*Compare* with investigations made in the dark field—p. 669.)

The "luminescence,"† or more strictly speaking "fluorescence," of rubber and rubber compounding ingredients when exposed to filtered ultra-violet light has been studied by several investigators in recent years. The results have demonstrated that observations of interest can be made either with or without the use of the microscope. M. Krahl [*Kautschuk*, **3**, 159, 180 (1927)] seems to have been the first to point out the possible value of the phenomenon of fluorescence to rubber technologists. Zinc oxides and accelerators seem to have constituted the major interests of those who have entered this

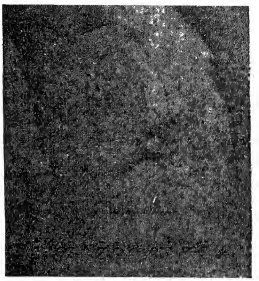
* Translator's Note. The terms "Aktivierung" and "aktive," which are frequently to be found (within quotation marks) in the German text, do not seem to have very satisfactory English equivalents. Although the literal translations, "activation" and "active," have sometimes been used, it should be kept in mind that the terms as thus employed do not have their usual significance. The sense is often that of "reinforcement" and "reinforcing" respectively.—V. N. M.

[8] See Wiegand and Braendle, *Ind. Eng. Chem.*, **15**, 259 (1923).

† Translator's note by V. N. M.

PLATE II, Group I. Inclined, reflected light. (Figures 1, 2, 3 and 4.)

Figures 1 and 2. Torn surfaces of "non-activated" (non-reinforced) and slightly reinforced stocks of inner tube type; (1) without (2) with tendency toward structure formation (cross graining at right angles to the direction of tear). Cf. p. 644. Dry preparation. Zeiss Planar, 35 mm.



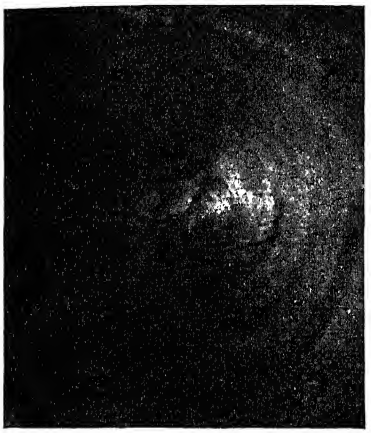


Fig. 3. Cross section of a vulcanizate composed of several layers (older solid tire type, containing about 70% magnesium carbonate and 10% litharge). Cf. p. 645. Paraffin oil preparation. Zeiss Tessar. Approximately natural size.

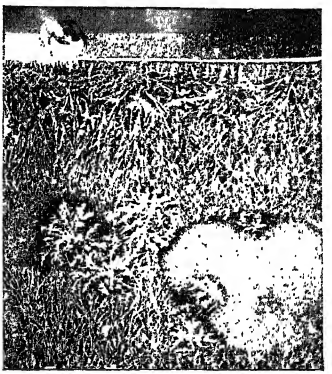


Fig. 4. Normal vulcanizate of crepe rubber and sulfur (10%), showing different crystalline forms of sulfur. Section cut with scissors at right angle to surface. Cf. p. 646. Paraffin oil preparation under cover glass. Zeiss Planar, 35 mm.

field. That different samples of zinc oxide give different fluorescent colors was demonstrated by P. G. Nagle [*Trans. Inst. Rubber Ind.*, **3**, 304 (1927)], F. Kirchhof [*Kautschuk*, **4**, 24 (1928)] and V. N. Morris [*Ind. Eng. Chem.*, **26**, 107 (1934)]. Kirchhof attributed the differences in zinc oxides largely to the impurities present, while Morris showed that variation in particle size can account for variation in the fluorescent effects exhibited by samples of zinc oxide obtained from the same source. A great many of the accelerators in common use exhibit characteristic fluorescent effects, as has been shown by Krahl, Kirchhof, Morris, Ditmar and Dietsch [*Chem.-Ztg.*, **52**, 388 (1928)] and Kojima and Nagai [*J. Rubber Soc. Japan*, **2**, 260 (1930)]. Antioxidants, which have been studied less extensively than zinc oxides and accelerators, have been found to give intense fluorescent colors in many cases. As a rule the fluorescent colors are markedly different from the colors of the antioxidants in ordinary daylight. Many of the common softeners also exhibit fluorescent colors, which enable them to be identified after they have been extracted from rubber products of unknown composition. Very few of the inorganic pigments used in rubber show characteristic fluorescent effects. The effect of the state of vulcanization on the fluorescence of rubber itself has been studied briefly by Krahl, by Morris, and by G. Bruni [*See* Cotton, F. H., *Rubber Age (London)* **12**, 307 (1931)]. In a paper which does not thus far seem to have been published, this latter investigator stated that, as cure progresses there appears a correlation between the ad-

vent of strong fluorescence and the appearance of optimum tensile strength. Morris, who failed to confirm this observation of Bruni's with accelerated stocks in general, found that the intensity of the fluorescence of rubber stocks is influenced by the concentration of pigments and of vulcanizing agents, and that the capacity of vulcanized rubber for fluorescing can be destroyed by exposing it to direct sunlight for a short time.

After removal of all impurities and bloom, the surface relief of the vulcanizates reveals information regarding the methods of vulcanization (for example, heating in molds having surfaces which are microscopically uneven, heating in the open, or heating in a water bath), which are in some cases accompanied by characteristic shrinkage effects in the surface. There is no relation between this shrinkage and the inner structure or composition of the mix (in the investigation of which, regular cut sections, or in the simplest cases, fractured or torn surfaces, are generally used). Kröger [9] has discussed the normal results obtained with fractured surfaces and the significance of these results in the analysis of the breaking process.

The normal picture obtained with somewhat overcured compounds is shown in Plate II, Fig. 1. A high relief structure parallel to the direction of tear is evident. The nature of such a torn surface is entirely different when a certain structural solidity (increased resistance to tear) becomes apparent. In the terms of rubber technology, this latter condition gives indication of reinforcement. A slowly torn surface of a highly concentrated zinc oxide compound is shown in Plate II, Fig. 2. In such cases, there appears, in addition to the above mentioned structure, a secondary one which is transverse to the direction of the tear. This latter structure, which is made evident by a fine graining effect, gives indication of a periodically interrupted breaking process. Each of the equi-distant bright zones of the graining effect is to be attributed to a microscopically fine "loosening up" of the structure, which immediately develops into a break under the influence of stretching. A breaking process of this type is to be observed in the case of a very slight degree of reinforcement. Even in examples of the most perfect formation of structure, such as are found in mixes containing the so-called "active" (reinforcing) pigments, a lamellar loosening of the structure at the torn surface is observed. Upon further vulcanization, this effect gradually disappears, and the picture obtained with a torn surface approaches that shown in Figure 1, Plate II.

Additional information may be obtained when a larger and sufficiently smooth surface is available for investigation. In such cases satisfactory longitudinal and transverse sections of vulcanizates cannot be made with a knife alone, since irregularities cannot be avoided. The surface should be polished with a polishing wheel. A true polish is not necessary for the examination, and is in fact almost impossible in the case of soft rubber goods. A coarse polishing paper is preferred to a finer one. During the last stage of the treatment a very slight pressure may be applied. It is not possible to avoid a rough and grainy condition of the surface in the case of the softer vulcanizates. By rubbing with ether, the condition of such surfaces may be improved to such an extent that examination with oblique reflected light (preferably in the cone from a powerful arc lamp) is readily possible.

By the proper application of pressure on the polishing wheel, it is possible to establish that a variation in hardness exists between the various layers which are apparent in the relief of the surface. Furthermore, the differences in the degree of swelling of different layers, upon exposure of the surface

[9] *Z. Elektrochem.*, **34**, 725 (1928).

to chloroform, indicates a structure made up of individual plates. In the case of vulcanizates with heavy bloom, the final irregular distribution of the sulfur bloom may indicate whether the larger cross-sections are well cured throughout, or whether an "after-vulcanization" has occurred at individual spots. Determinations of this kind can even be made on non-blooming vulcanizates (at least the brightly colored ones), if the investigation is undertaken on fresh surfaces under ultra-violet light. (See "Investigations in the dark field.") This method of preliminary investigation is especially suitable for use with harder vulcanized products, such as solid tires, rubberized fabrics of airships, and the rubber layers on metal rolls or cylinders.

If an attempt is made to reveal finer details of the inner structure of this same preparation by employing a somewhat higher magnification, it becomes evident that only a small portion of the incident light enters at such an angle as to be of service in producing an image of particles lying under the surface. The major portion of the light is reflected at the microscopically uneven surface, and is lost as far as the image is concerned. This magnification consequently reveals not only the details beneath the surface but also those of the surface structure itself, and is therefore not highly valued for the purpose in view. Even smaller and apparently perfectly smooth surfaces, prepared by cutting with a knife, show this same tendency to reflect much of the light; and pictures of them, obtained when using "metallographic" illumination, show the above mentioned defect to a greater or less extent.

In order to obtain a better path for the beam of light, it is recommended that the surface of the sample be painted with a clear "lacquer" which has about the same refractive index as rubber, and which can be smoothed by laying a cover glass on it. The simplest transparent layer is clear paraffin oil, which is not appreciably absorbed by rubber. For permanent samples, Canada balsam may be used. In employing this material, both the cover glass and the balsam itself should be applied warm. When such a coating has been used, the obliquely incident light penetrates sufficiently to make possible a deep view of the specimen. Such preparations thus show whole series of phenomena which could not previously be made apparent. The examination of compounds with a high content of magnesium carbonate, for example, reveals the typical streaming figures with silky luster (and the corresponding anisotropy). (*See* Plate II, Fig. 3.) Such preparations also bring out the characteristic structure of black vulcanizates, when they consist of laminated layers of different carbon black compounds. That the penetration of the light is improved in the case of preparations of this kind is apparent from the fact that the various Tyndall effects, characteristic of different kinds of black, can be shown. By way of example, the examination of the cross sections of certain solid tires has proved them to contain gas black only in the outer layer. Similarly, the tread of a tire of English manufacture was found to contain gas black only in a thin outer layer. On the other hand, a recently examined tire of American origin was observed to be free from gas black in the outer layer only. Such distinctions by means of refracted light are impossible with dry preparations.

The very simple method of preparation and observation under reflected light is consequently in many cases a worthy supplement to other processes. This procedure consists of the preparation (with knife or scissors) of freshly cut surfaces (the size of which is determined by the amount of magnification

desired), the wetting of these surfaces with paraffin oil, and the covering of them with a cover glass. The difficulty arising from an insufficiently smooth surface may be overcome by inclosing the preparation (with paraffin oil on its surface) in the press made of plate glass (*see* p. 639), and observing it through the top plate. This arrangement (usually in combination with objective T3) produces excellent pictures, and can be used with grazing incident light. The typical crystallizations of sulfur which are observed in vulcanized rubber-sulfur mixes become visible with this arrangement, as do also the disturbing separations of sulfur which appear on sections taken from solid tires. The flow lines and calender effects (grain) in vulcanizates containing a smaller proportion of compounding ingredients are also made evident under these circumstances. The results of certain investigations of rubber-sulfur mixes have already been published.[10] In Figure 4 of Plate II is shown another picture of a normal vulcanized mix (90 per cent crepe and 10 per cent sulfur). It is especially instructive to observe the somewhat characteristic dependence of sulfur separation on the degree of vulcanization of the compound. This can be seen in a mixture which has been cured in a mold, one side of which was kept cool during the cure. In the cross section of such a sample, all steps of the curing process may be observed side by side.

In case investigations with higher magnification are to be conducted, it is impossible to avoid the use of a vertical illuminator. With dry specimens, the picture obtained in perpendicular reflected light is almost exclusively one of the surface alone. Since such a picture is generally of little interest, immersion objectives are used. In case the swelling action of the immersion oil does not interfere, observations can be made directly without cover glass.

By applying metallographic methods to the examination of rubber fabrications,* F. H. Roninger [*Ind. Eng. Chem., Anal. Ed.*, **5**, 251 (1933)] has recently accomplished something which certain previous investigators had attempted with little success. The sample, preferably after vulcanization, is cut with one suitable face roughly plane, and is then immersed in a bath of molten sulfur at 135° C. for 12 to 24 hours. After having been cooled, the sample will have a surface layer (several millimeters thick) of a tough horn-like consistency too hard to be dented with the finger nail. For the grinding and polishing of the hardened sample, an automatic polishing machine, a simple variable-speed polishing lap, or other device can be used. The sample is flattened on a coarse silicon carbide grinding wheel, given a rough polish on a wheel covered with wool broadcloth charged with a paste of "600" silicon carbide, and finally polished on a wheel covered with cotton-backed silk velvet charged with a small amount of a special magnesium oxide (Shamva) in water. After flooding the surface with water to remove all the powders, the sample can be examined and photographed, using any good vertical illuminator and short-mount objectives. The most useful application of this method has been in the quantitative estimation of the degree of dispersion of pigments in rubber mixes, particularly tread stocks.

Investigations by Transmitted Light

Microscopic examination by transmitted light is made possible by the fact that the rubber substance in a thin section of the vulcanizate is a practically transparent, structureless, and colorless body, in which all added materials can be seen, unless they have become dissolved or have a refractive index too close to that of the rubber. The usual treatment of the sample with a swelling agent, as well as the embedding of it in paraffin oil or Canada balsam, only tends to make the image of the added materials better by virtue of making the rubber clearer. Evident distortion of structure caused by the swelling agent occurs only when the compounding ingredients are "fixed" in the rubber by a chemical reaction. Distortion of this kind, which occurs in the

[10] See *Kolloid-Z.*, **39**, 1 (1926).

* Translator's note by V. N. M.

presence of active agents, such as the oxides of lead, calcium and magnesium, leads to the "breaking down" of individual particles during the swelling. The vulcanizates of older types became opaque through the copious crystallization of free sulfur. Much less trouble from this source has been encountered since the introduction of accelerators to the industry. The many colors introduced into the vulcanizates by the accelerators themselves do not cause any trouble during observations on thin sections.

Compounds which are of simple type, and in which various compounding ingredients may be observed in their characteristic forms, are encountered in the field of inner tube manufacture. Pictures of such compounds are shown in Plate V. (*See* p. 666.) These pictures make the rubber medium appear to be as clear as glass, and enable the relative sizes of the added materials to be easily seen. On Plate V are shown pictures of a dye which is molecularly dissolved (Fig. 19), of colloidally dispersed antimony pentasulfide, most of which cannot be resolved (Fig. 15), of zinc oxide and antimony trisulfide, which are optically resolvable to some extent (Figs. 16 and 17), and finally of the coarsely ground lumps of factice, chalk and gritty magnesia usta (Figs. 18 and 20). These coarse ingredients play the rôle of foreign bodies and can be easily loosened from the combination by a marked swelling of the sample. Although agglomeration tends to take place with many of the pigments themselves, the mixing process is such as largely to avoid agglomeration of these pigments in rubber compounds. Consequently, the pigments generally appear in the rubber as individual (primary) particles, isolated from one another. Examination with high magnification but at limited depth, as was the case with the pictures shown in Figs. 15 to 20, reveals relatively broad rubber bridges between the particles, but no definite tendency toward orientation.

Dispersion greatly different from the types shown in Figures 15 to 20 indicates either a compounding ingredient of low value or an unusual mixing process, such as one in which the "warm up" period has been insufficient. Manufacture directly from latex also gives products with unusual dispersion of pigments. Although it is possible to make conjectures regarding the identities of various pigments in goods made from latex, it is scarcely possible to identify them microscopically on the basis of a characteristic dispersion. This lack of a characteristic dispersion arises from the fact that the pigments are to some extent undispersed and to some extent coagulated. (*See* Plate IV, Figs. 13 and 14, p. 665.)

The tendency for the individual particles to remain separated from one another in rubber compounds prepared in the usual manner is also maintained in the case of submicroscopic particles, as is illustrated by observations made on tread and solid tire compounds containing gas black (Plate III, Figs. 7 to 9). In the background of the microscopic field (in the case of such compounds) there appears a fine "granulation" which cannot be resolved. This "granulation," which shows the red-brown color of colloidal solutions, can be readily distinguished from the dispersion of gas black brought about by rubbing it with oil or resin. Coagulation phenomena during vulcanization are not demonstrable (Fig. 7). The typical effects observed during the physical testing of such vulcanizates are therefore probably not to be considered as resulting from the coagulation of the black, but are rather to be explained on the basis of structural phenomena, such as have recently been observed to a considerable extent. Compounds of this type

exhibit a fine lamellar structure, which can be made visible by the mechanical stressing (squeezing or crushing) of a thin section. A typical result is shown in Figure 6, Plate III. From this figure it is obvious that the gas black "granulation" and the lamellar structure are not disturbed by the presence of the larger zinc oxide particles. The tendency for the finer and coarser particles to remain separated from one another is apparent in Figures 8 and 9, Plate III, in which it is possible not only to detect the coarser particles of zinc oxide, lampblack, and thermatomic black microscopically, but also to estimate their relative proportions if necessary. In this latter case the study must be made on a photomicrograph taken through a net-ruled eyepiece micrometer. (Figs. 8, 9.)

The characteristic degree of dispersion of various compounding ingredients (as revealed by the microscope) is already partly known from the publications of other investigators, and has been reproduced in various vulcanizates of decidedly different origin. For the purpose of microscopic analysis it is desirable to divide the ingredients into organic diluents (factice, for example), pulverized minerals and accelerators, and finally those active and inactive pigments which are of such a size as to be optically resolvable. This classification has been employed in the discussion which follows.

Preparation of Thin Sections

Certain difficulties encountered in the preparation of sections suitable for investigation by means of transmitted light probably account for the fact that many of the studies undertaken in this field have remained incomplete. These difficulties arise partly from the natural resistance of the samples toward cutting, and partly from the variable nature of the vulcanizates, which may have properties anywhere between those of elastic soft rubber and those of inelastic hard rubber.

The stiffness required of a satisfactory sample can be obtained either by means of the action of the vulcanizing agents, or by incorporating a high proportion of pigments, or finally by a combination of both of these procedures. This variation in the possible methods of procuring the desired stiffness provides still another reason why samples vary in regard to the ease with which they may be prepared for examination. Consequently, there is no standard method at the command of the microscopist. The surmounting of these difficulties, however, necessitates no greater manual skill than that which is successful in applied microscopy in the fields of botany and zoology.

The hard rubbers and the vulcanizates approaching them in hardness constitute the class easiest to prepare for examination, provided they are not so loaded with coarse fillers (cotton, pumice, etc.) as to crumble when cutting is attempted. With such samples, usable sections can generally be obtained merely with a knife, or, more strictly speaking, with a scalpel or razor. The procedure consists of cutting the finest possible shaving, while keeping the blade parallel to a previously prepared surface. If the vulcanized sample is sufficiently transparent, the constituents are all discernible in thin sections, and it is apparent that the examination of sections having larger dimensions is unnecessary. During examination, the sample is usually mounted in chloroform, benzene, toluene, etc., and is held between cover glass and slide in the customary manner. In the case of permanent preparations, the sample may be embedded in Canada balsam. The disadvantages of Canada balsam are that the swelling effect of the above-mentioned organic solvents is not obtained, the zinc oxide particles may dissolve, and the dyes in the rubber

PLATE III, Group II. Transmitted light. (Figures 5, 6, 7, 8 and 9.)

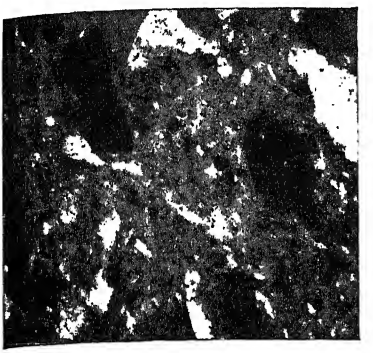


Fig. 5. Heel stock, containing light and dark pulverized vulcanized scrap. (Cf. p. 655.) Thin section. Zeiss apochromat, 16 mm.

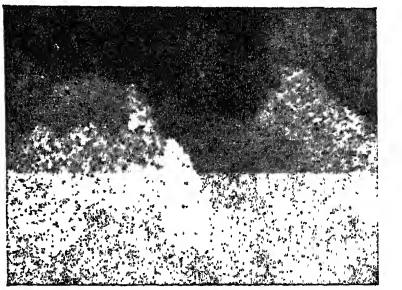
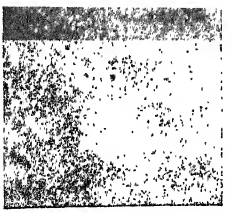
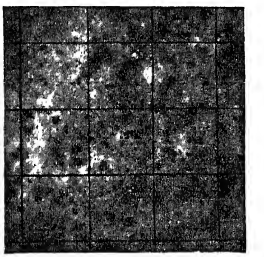
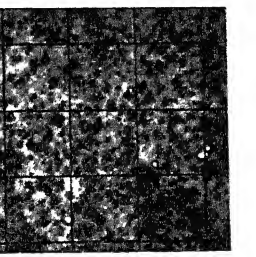


Fig. 6. Solid tire stock containing gas black. Lamellar separation resulting from squeezing of the thin section. (Cf. p. 648.) Leitz—1/7.







Figures 7, 8 and 9. Tread stocks (7, 8) and solid tire stock (9). "Granulation" due to entirely submicroscopic gas black (7). Stocks containing both gas black and various proportions of lampblack of larger particle size (8, 9). (Cf. pages 647 and 662). Thin section. Zeiss apochromat, 2 mm.

may fade. (*See* p. 654.) The unavoidable irregularities in a sample cut by hand are not very evident in brightly lighted and slightly swelled material. There should be no occasion for confusing these irregularities with those resulting from the structure of the sample itself. The irregularities resulting from the method of sectioning can be made even less apparent by careful adjustment of the condenser diaphragm. There is consequently no necessity for preparing "mineralogical thin sections" with polished and carefully leveled surfaces.

The preparation of transparent sections of flexible vulcanizates or soft rubber goods is not so easily accomplished, although preparations can be made in a manner different from that described above. It appears from the literature that other investigators have suited their method of preparation to the character of the material which happened to be the object of their investigations. In the most favorable cases, it has been observed that the examination can be made without making thin sections, since the treatment with paraffin oil or other swelling agents gives a satisfactory transparency. This method is satisfactory for thin vulcanizates having low pigment content (cut sheet, for example), as well as for dipped or spread layers from which the fabric foundation has been removed. The influence of the mounting medium on the nature of the transmitted image is quite evident in the case of prepara-

tions of this latter type. When mounting in paraffin oil, the surface structure (resulting from the laminated condition of the stock) becomes almost invisible, as do also talc and other powders on the surface. The examination can consequently be extended to the inner portions, where air bubbles, impurities of all kinds, and crystals of sulfur and of accelerators are to be found. (Use is made of the same optical principle in the investigation of paraffin oil preparations in reflected light, as discussed on p. 645.) In the case of relatively large vulcanizates with low pigment content, such as slabs and tubes, satisfactory specimens can be prepared merely by cutting thin sections (0.5 to 1.0 mm. thick) with scissors. Such sections become transparent when mounted in paraffin oil or certain other media. It is not desirable to wet either the blade or the rubber before cutting. Immersion in paraffin oil after cutting is necessary, not only for optical reasons, but also in order to bring any distorted edges back to their original positions. The distortions of the surface resulting from cutting with scissors disappear when the specimen is mounted in paraffin oil. Pressing the cover glass on the sample or inserting the latter in the plate glass press afford useful mechanical means of obtaining smoother samples and consequently better pictures.

In the investigation of vulcanizates containing higher percentages of pigments, the requirements with respect to the preparation of the sample are more rigid. The thickness of the section examined must be governed by the pigment content, if useful images are to be obtained. In the case of a whole series of heavily loaded stocks (in which the gas black content may be as high as 80 per cent), it is often necessary to reject a large number of individual slices before a satisfactory section can be found.

In the first attempts at the preparation of samples from vulcanizates of this type, use was made of a razor blade. The cutting is done by hand in this method, water, glycerol or oil being used to wet the blade and thus assist the operation. Although the cutting edge is moved back and forth without special pressure, it is desirable to support the rubber sample from beneath and also from one side if possible. Pressure on the razor blade tends to cause the edges of the cut to turn in and the blade itself to slip, especially in the case of highly elastic vulcanizates. Despite the greatest care, the sections obtained are usually wedge-shaped. It is only around their edges that parts suitable for microscopic examination are to be found.

As a consequence of these difficulties the more modern investigators, such as Depew and Ruby, Green, and Ames (*see* p. 637), have confined their efforts to mechanical methods of cutting in which the microtome is used. When employing this instrument, it is necessary to give the vulcanizate a special preliminary treatment in order to provide it with the consistency and degree of hardness necessary for cutting. For this purpose, Depew and Ruby used the ordinary histological method of freezing, and thereby avoided any possible chemical alteration of the microscopic image. This advantage makes their method indispensable under certain circumstances.

For hardening his samples, Green used a dilute solution of sulfur chloride, which is said to impart a paraffin-like consistency to the sample when properly handled. Since this type of hardening results from after-vulcanization, it is necessary not only to determine the necessary quantity of sulfur chloride by preliminary experiments, but also to keep the quantity of the agent and the size of the sample constant, if results are to be duplicated. A solution of sulfur chloride in carbon tetrachloride serves very well for the treatment

of reinforced compounds of the tread stock type. For more elastic compounds, such as carcass stocks, a solution in carbon disulfide may be used. For a preliminary examination, the concentration of sulfur chloride may be 15 drops in 50 cc. of solvent in the first case, and 5 drops in the second. The time required for the reaction, which is influenced by the presence of accelerators in the compound, varies from one hour to several hours. The hardened piece is finally embedded in paraffin, and fastened on the microtome in such a manner that one edge is in contact with the knife. Experience has demonstrated that the quality of the cut section is influenced by the angle between the blade and the direction of motion and also by the angle of approach to the sample. These angles must be carefully fixed, if good results are to be obtained. Since satisfactory adjustment of the cutting blade is possible with the microtome, this costly instrument is recommended.

Judging by the published results, it seems that both methods give quite uniform and transparent sections. With the sulfur chloride method, as Green himself mentioned, care must be exercised in the interpretation of the structures observed, since they are sometimes influenced by the hardening agent used. Mention should also be made of the occurrence of honeycomb structures, which resemble the structures of fixed histological material, and which did not exist in the original rubber sample. Such structures, which probably develop as a consequence of the treatment with melted paraffin, constitute an undesirable source of error in the case of estimations of the degree of dispersion of fine pigments. There also appears to be evidence of coagulation phenomena, which may have some connection with the above-mentioned secondary structures. For instance, relatively large aggregates, which do not appear under other conditions, and which are not characteristic of the pigment concerned, were found in gas black compounds by Green and also by Ames.[11] As a consequence of this observation, Ames attempted to improve the freezing process as much as possible. He introduced the use of a freezing box to eliminate the difficulties which existed in the older procedure of Depew. The results published by Ames were obtained with compounds which were of such a nature as to place few requirements on the method used for the preparation of microscopic specimens.*

Although the results obtained furnish no reason for its rejection, the microtome has not been very generally adopted for microscopic work of this type. Since this apparatus is not available for general use, the discussion below will deal with preparations made by hand. Good results are obtained with this older method when use is made of a "double" knife, consisting of two blades firmly fastened together in parallel planes (and ground plane-concave). The "double" knife of Orth (or of Schieferdecker), which has blades about 6 cm. in length, takes a section from the main body of the piece of rubber, rather than from the upper surface or from an edge, where the possibility of the knife's slipping would be greater. In case both its sides are uniform and evenly ground, the knife may be placed on the rubber without pressure and allowed to penetrate while being moved back and forth. The penetration is facilitated by wetting with paraffin oil, glycerol, and the like. The depth attained before separation of the section occurs depends on the distance between the two blades of the knife. As a rule, a section 0.5 mm. or less in thickness is sufficient to permit of an insight into the composition

[11] *J. Roy. Microscop. Soc.*, p. 265 (1923).

* Translator's Note. A recent development in connection with the preparation of frozen sections is that of T. F. Steele, [*Ind. Eng. Chem., Anal. Ed.*, **2**, 421 (1930)] who has worked out a method for mounting rubber in basswood and freezing it with liquid air before cutting it with a microtome.—V. N. M.

of the mixture. The material should preferably be cut beforehand into sections of appropriate size (about 2x4 mm. in cross section). The section which is between the blades when the knife is withdrawn can be removed by a probing needle without dismantling the knife.

In order to decrease the deformability of most soft rubber products, it is recommended that the sample chosen be allowed to swell in chloroform for several hours before cutting. When the maximum quantity of chloroform has been absorbed, the sample possesses an inelastic consistency which is much more suitable for the preparation of sections. This method possesses an additional advantage in that the absolute thickness of the section is actually less as a consequence of the swelling which has occurred. Since samples prepared in this way tend to dry out rapidly during cutting, the surface should be covered immediately beforehand with paraffin oil, which retards evaporation of the chloroform for some time.

When used without modification the method just described gives satisfactory results with pure gum or lightly pigmented compounds, such as carcass and inner tube stocks, or those made from latex. Moreover, it is also suitable for use with unvulcanized mixtures, since the sticking of the knife to the rubber is not to be feared when paraffin oil or glycerol is present.

In the case of stocks of high pigment content, such as tread or solid tire stocks, a special subsequent treatment must be given the sections. Relatively good transparent sections of gas black stocks (containing about 30 per cent of black) can be prepared by this method, since such stocks are penetrated by reddish yellow light to a surprising degree. The difficulties are considerably greater in the case of mixtures containing 30 per cent of lampblack, since their resistance to cutting is much greater. In making preparations from stocks of this type, the knife blades are set especially close together, and repeated cuts are made in the surface of the previously swelled material in order to make available a larger choice of sections.

Apart from this method, details may be revealed at the highest magnification only by stretching the cut material to such an extent that it becomes transparent and then mounting it in this condition (in the manner already described by Green).[12] The necessary stretching is obtained by pressing the section between cover glass and slide in the plate glass press. Only the best sections are used. They are mounted in chloroform and heated to about 70° C. during the pressing. After several hours, the preparations, which have dried in the press, are removed. No change in thickness occurs upon removal. In case permanent preparations are desired, Canada balsam may be placed around the edges of the cover glasses and warmed so that it will form a seal for the samples.

Preparations just as good as those obtainable by the method just described can often be made by embedding the section (cut from the material swollen in chloroform) directly in Canada balsam in the usual manner. If sufficient pressure is applied just before the balsam solidifies, the sample can be immediately fixed.

R. P. Allen [*Ind. Eng. Chem., Anal. Ed.*, **2**, 311 (1930)] has recently described a useful method for the preparation of micro-sections of rubber stocks.* A triangular ridge is first cut on the edge of the sample to be examined. With a small pair of dissecting scissors a tiny sliver of rubber is cut from the crest of the ridge. The very tip of this sliver, which should be barely visible to the naked eye, is then cut off for use. The piece must be so small that subsequent squeezing will not cause extreme distortion of

[12] *Ind. Eng. Chem.*, **13**, 1130 (1921).

* Translator's note by V. N. M.

agglomerates or destroy the relation of one particle to another. After carefully placing the minute piece in the center of a small drop of rosin or beeswax which had been previously melted on a slide, the rosin is remelted and then covered by means of a cover glass. The rubber is then squeezed out thin by pressing on the cover glass with two suitably shaped pieces of wood, such as the handle of a small scalpel. The pressure is maintained until the rosin hardens. Even in the case of stiff stocks, it is possible by this method to make sections less than 1 micron in thickness.

Finally, it should be mentioned that the double knife can be used in the preparation of sections from larger articles which are reinforced with fabric, such as pneumatic tires. Such preparations can be examined by transmitted light, provided the rubber stock itself is not too opaque. Not more than two or three layers of fabric are cut at one time. After the sample has been laid on a piece of cork (so that the knife will not be damaged), the section is cut in one motion by drawing or pressing the knife through the sample. The blades are not to be set too close together, since in very thin sections the cords which are cut fall apart and the cohesion of the preparation as a whole is lost. Moreover, preliminary swelling is not permissible, as it also tends to cause separation of rubber and fabric. Swelling with chloroform or similar agents is particularly objectionable, since such agents tend to displace the air from air bubbles in the fabric. This air was not displaced by the rubber during manufacture of the article, and should therefore not be overlooked during the microscopic study. The recommended procedure is to embed the preparation in glycerol. A picture obtained with a preparation of this kind is shown in Figure 10, Plate IV, page 665.

When the nature of the contact surface between fabric and rubber is to be studied under higher magnification, a thinner section involving only a single cord may be used. Such sections can be cut with the knife, preferably without using pressure. When the section includes only a single cord, rubber will remain with the cord only at the points where the fabric is actually wetted by or fixed in the rubber. A large part of the rubber does not stay with the fabric in such a preparation, since there is but little genuine impregnation or adsorption involved, and the attachment of rubber to fabric is largely only a superficial one. The same situation also exists in the case of articles made from latex. (In this connection, *compare* Fig. 11, Plate IV and Fig. 23, Plate VI.)

Microscopic Studies of the Various Ingredients in Rubber Compounds

Color Reactions of Pigments and Filling Materials

Microscopists working in the field of biology have introduced a large number of micro-reactions which are very valuable when used as identification tests for particles of microscopic size. In fact, the series of reagents which may be used for this purpose in the case of compounding ingredients in rubber stocks is capable of considerable extension. On the basis of the assumption that the penetration of the dye used as indicator is due to its solubility in vulcanized rubber, oil-soluble reagents have been much in favor. Among the more useful reagents may be mentioned one per cent solutions of alizarin or alkannin in alcohol and chloroform. Such solutions are capable of revealing interesting basic constituents by the process of forming lakes. If the solvent mixture used contains 3 parts of alcohol for each part of chloroform, the rate of penetration of the sample by the solution is quite rapid. The time required for dyeing amounts to about 5 minutes, although

it varies somewhat with the composition of the sample. Characteristic lakes are formed by individual particles of magnesia and lime, particularly with alizarin. This reagent also forms diffuse colors in the presence of magnesium carbonate and zinc oxide, as is apparent in Plates IV and V. There is often a selective coloring of the white particles of embedded factice, which is probably to be attributed to the bases present in the latter. The zinc lake appears to best advantage when a small amount of chloroform is added. A lake with magnesium carbonate does not form when the stock contains a high proportion of compounding ingredients and is over-vulcanized. Since basic accelerators, which are never completely consumed during vulcanization, also tend to give color reactions, it is preferable to wash the section with alcohol and chloroform before testing for metallic oxides.

A less sensitive reaction for the detection of basic constituents is that obtained by the use of a solution of eosin (in the form of the free acid) in ether. By means of this reagent, magnesia and lime can be distinguished, as they differ in the degree of fluorescence which results. This test is not to be highly recommended, since an ultramicroscope is required and much time is necessary. Permanent preparations can only be mounted in a glycerol-gelatin medium, since Canada balsam dissolves the lake and causes the color to change.

For an adequate interpretation of microscopic observations, it is necessary that the microscopist be just as familiar as possible with all of the compounding ingredients which may be encountered. Ability to recognize the characteristic particle shapes and particle colors comes only by experience, and should be developed by means of preliminary experiments. As is customary in biological studies, it is desirable to set up for subsequent comparison a complete series of standard permanent preparations, each of which contains a single typical pigment in masticated, unvulcanized crepe rubber. In the case of zinc oxide, a concentration of 6 per cent is suitable. With other compounding ingredients, the concentration chosen may be greater or less than 6 per cent, depending on the specific gravity and degree of fineness of the ingredient. Permanent preparations can be made merely by pressing a small sample (having a volume of about 1 cubic millimeter) between a cover glass and a slide in the plate glass press. The pressure must be sufficient so that a layer of satisfactory transparency is obtained. Technical mixes of known composition may also be used in the preparation of standard samples for comparison, after they have been "diluted" with a suitable proportion of masticated crepe. A set of standard preparations of this type enables the microscopist to become familiar with many phenomena which might appear very unusual if observed for the first time during the microscopic investigation of an unknown product.

Characteristic Forms in Which Organic Diluents Appear in Rubber Compounds

Factice (oil substitute) is not soluble in rubber, but is found in large or small lumps of angular or spherical shape. The form and size of the particles depends upon the degree of vulcanization of the factice, or upon its hardness and the consequent ease with which it can be pulverized. Since the index of refraction of rubber varies so little from that of the oil substitutes, the latter can be recognized in a rubber stock only after careful regulation of the diaphragm of the condenser. Factice having a high sulfur content

can be more easily recognized, as a consequence of its brownish yellow color. (*See* Figs. 16 and 20, Plate V, p. 666.)

Mineral rubber contains insoluble gritty constituents which may be distinguished from factice on the basis of their greater fineness and more intensive brown color. The appearance of mineral rubber in rubber stocks is illustrated in Figure 10, Plate IV and Figure 23, Plate VI.

In the investigation of mixes containing reclaimed rubber, it is observed that particles of rubber which have not been regenerated are present in nearly all types of "reclaim." These particles of powdered, vulcanized scrap are as large as or larger than the particles of factice. Often the presence of reclaimed rubber in a stock can be proved only by the presence of these particles, as other definite indications may be lacking. Such is frequently the case in the carcass stocks of pneumatic tires, for instance.

The identification of finely powdered vulcanized scrap is possible on the basis of the amount found present, and also in most cases on the basis of the great fineness which these particles must usually have in order to produce the desired effects. Additions of this type can also be detected, when stocks containing them are made into cements. In many cases, some conspicuous filler in the powdered scrap can be recognized. Thus in cheap red stocks containing tube scrap colored with golden antimony, the yellowish red color of the antimony pentasulfide becomes apparent by transmitted light. Identifications on this basis are also often possible when the scrap contains zinc oxide, carbon black or certain other pigments. In Figure 5, Plate III, is shown a thin section from a heel stock. The striking color of a section containing antimony pentasulfide is illustrated in Figure 15, Plate V.

Characteristic Forms in Which Minerals Appear in Rubber Compounds

Characteristics by means of which the coarser pulverized minerals can be recognized microscopically in vulcanized rubber are not as prominent as in the case of organic diluents.

Sulfur particles can be detected in a freshly prepared stock as a consequence of their high index of refraction and their sharp contours. The sizes and shapes of the particles change, however, even when the stocks are merely stored for a long time in the unvulcanized state. (A growth of large crystals at the expense of small particles occurs.) During the vulcanization of mixes having relatively low sulfur contents, the sulfur may disappear entirely from the field of view. Among finished products, it is only in hard rubber compounds which have not been properly vulcanized that sulfur particles may be found in their original form. In other vulcanizates (particularly that type without accelerators, which was formerly very common), the unused sulfur appears in time as a more or less dense crystallization. This crystallization, which has often been pictured and described in the literature, permits certain conclusions to be drawn regarding the degree of vulcanization and the presence or absence of accelerators.

Litharge, which appears in unvulcanized mixes in the form of yellow or reddish-yellow particles having a plate-like structure, becomes difficult to recognize in vulcanized stocks, in which it forms black lead sulfide. Nevertheless, identification is possible as a consequence of the characteristic "halo" of lead sulfide which forms around each particle of litharge. An intense yellowish-brown to brownish-violet color by transmitted light is apparent

with litharge in the case of mixtures containing accelerators. A less striking coloration is to be observed in the presence of magnesium carbonate (in the solid tire stocks of several years ago, for example). Colors deviating from those with other accelerators are present in mixes containing Vulkacit P (piperidinium pentamethylenedithiocarbamate).[13]

The individual particles of other pulverized minerals which find use as fillers in rubber stocks do not always exhibit characteristic forms or colors. As a rule the finer particles cannot be determined, and it is only with the coarser particles that microscopic methods can be used with any assurance of success. In mixes containing either infusorial earth or the so-called marine chalk, the well-known natural forms of these materials can be recognized. For the detection of infusorial earth (in tennis balls of English manufacture, for instance), a relatively high magnification and careful adjustment of the condenser diaphragm are necessary. Particles of heavy spar (barytes) can be recognized by the arrangement of the fractured edges (as in repair patches for treads), while powdered glass is characterized by the shattered and rounded particles, and corundum by a blue-black coloration.

Talc is also of interest, since this material is to be found in almost all vulcanizates, especially those made wholly or in part from compounds which have been processed considerably. Relatively large needle-shaped particles may be seen, provided they are lying edgewise in the thin section being examined (section from a bicycle tube, for example). The identification of talc is seldom a matter of importance, since the quality of the stock is generally not appreciably influenced by the presence of this material.

There is no definite characteristic by means of which the different kinds of kaolin can be identified. The finest particles, which must be present if kaolin is to produce the effect expected of it, cannot be seen by transmitted light, while the larger gritty particles have irregular and varying shapes. Only with certain grades of English origin is there a characteristic form (fan-shaped) which may be used for purposes of identification.[14] (*See* Fig. 14, page 665.) The difficulties encountered with other powdered silicates, which are often present only as carriers for organic dyes, are similar to those with kaolin. A qualitative microscopic analysis of the individual mineral particles in a stock (especially when a mixture is present) cannot be made without the help of a polarization microscope.

In fact, the determination of the degree of fineness of the visible mineral particles is generally more important than is the qualitative analysis with the polarization microscope, since the effects produced by the minerals are usually determined by their fineness, rather than by any of their specific properties (such as particle shape, for instance). Schippel[15] observed microscopically that particles of barytes are in loose contact with the rubber substance, and become separated from the latter during elongation of the vulcanizate. The same has since been found to be true for various minerals with different degrees of fineness. Notable exceptions include litharge, lime and magnesia, the particles of which seem to be more firmly fixed in the rubber after vulcanization than before. This behavior of the minerals enables a microscopist to isolate them during the swelling of the preparation in chloroform. Even the finer individual particles of kaolin, chalk, etc., in the swollen section are found to be either surrounded by an empty space or entirely separated from the section. A typical porosity in the stock, corresponding exactly to the

[13] See Pohle, *Kolloid-Z.*, **39**, 1 (1926).
[14] Dick, *Mineralog. Mag.* (1908).
[15] *J. Ind. Eng. Chem.*, **12**, 33 (1920).

shape of the particles, is thus produced. This effect is also to be observed in unvulcanized mixes, and is likewise encountered during the microscopic examination of torn surfaces. The study of torn sections shows that even particles of sulfur and of accelerators may easily become loosened from the rubber matrix. An explanation is thus provided for many troubles encountered in vulcanization (those occurring with so-called "air-curing," for example).

The effect of the mineral particles, which consists in a more or less complete "loosening up" of the vulcanizate, is not much different from that of any foreign body. The extent of this effect is best revealed by a determination of the average particle size. The shape of the particle seems to play a minor part, and is a matter of significance only in the case of talc. An approximate determination of the maximum or average value of the particle size can be obtained by use of objective and ocular micrometers. Since so many particles are lost in cutting a section, the recommended procedure is to make use of a preparation consisting of grindings, when determining the particle size of the minerals in a heavily compounded stock. A knowledge of the degree of fineness is valuable when it is desired to imitate an unfamiliar stock in the matter of resistance to rubbing, grinding, or wear. It has been established that the degree of fineness of the minerals in a stock exerts an influence on the cutting blade of the bias cutter or similar machine. An interesting relation between the porosity of inner tubes and the particle shape and maximum particle size of the talc in the stock has also been found to exist.

Since the various manufacturing concerns have different specifications with regard to the degree of fineness or of pulverization of the minerals used, it is not worth while to present the results of very much microscopic work on such minerals. The maximum particle size of the minerals found in various rubber products is usually about as follows:

Powdered heavy spar (barytes)	0.05 mm.
Powdered mineral chalk	0.09 to 0.12 mm.
Marine chalk	0.05 mm.
Powdered kaolin	0.12 mm.
Talc	0.25 mm.

In order to make satisfactory comparisons, it is obviously necessary to bring the two objects into the same field of view at the same time. This can be done either by use of a comparison microscope with two tubes or of a comparison ocular as a bridge between two individual microscopes (made by Leitz or Zeiss). As far as the preparation of thin sections of vulcanizates or of other specimens is concerned, practically the same conditions must be maintained for a comparison preparation (including both unknown and standard) as for a single preparation. This matter has already been discussed in connection with the testing of raw materials.[16] The adjoining thin sections of vulcanizates or specimens from unvulcanized mixes are so placed between slide and cover glass that a sufficiently sharp line of contact can be obtained by the application of pressure. When this line of contact is brought into the middle of the field, it is possible to determine any fine differences in color tone or in turbidity which exist between the two sides of the field of view. In the evaluation of these comparison preparations, it is advantageous to keep in mind the photometric assumptions which are applicable to such a "half shadow" comparison. The investigation should be made at the lowest possible magnification, since the more highly magnified view of single par-

[16] Pohle, *Z. wiss. Mikroskop.*, **44**, 183 (1927).

ticles does not permit the boundary line to be discerned with exactness. As a further requisite, only preparations showing a distinct line of contact should be used. The boundary line shown in Figure 21, Plate V, is a very unsatisfactory one. In some comparisons, it is desirable to increase the concentration of the minerals, since the sensitivity of the comparison increases with increasing concentration. The specific gravity is not the only criterion for deciding on the amount of a coarse pigment or powdered mineral which should be put into a stock when it is desired to duplicate the characteristic appearance of the fillers in rubber. The degree of fineness must also be given consideration. The concentration of the fillers in technical vulcanizates is usually high enough so that a sensitive microscopic comparison can be made between the unknown product and a duplicate compounded on the basis of a chemical analysis.

Since the concentration of compounding ingredients and the thickness of the section can be adjusted so as to be the same on both sides of the line of contact in a comparison preparation, it is possible for differences in the coloring power or the covering power of the fillers to be revealed. A finer state of pulverization leads to an increase in the covering power; that is, an increase in the turbidity of the specimen. The coloring power of colored fillers is naturally greater when the fillers have been more finely ground. Since the intensity of luminous radiation is somewhat dependent upon the fineness of a powder, differences in the fluorescent effects observable when examining two samples by reflected ultra-violet light may be traced to differences in the degree of fineness of the fillers present. By having available sulfur, ultramarine, litharge, chalk, etc. in different degrees of fineness, the specific characteristic form in which a given mineral occurs in an unknown stock can be readily determined.

Characteristic Forms of "Active" and "Inactive" Pigments*

Usable pictures of the characteristic forms of such of the finer pigments as are completely or partially resolvable in the microscope can be obtained by means of comparison preparations of the type discussed above. Compounds suitable for such studies include those containing such pigments as the commercial varieties of clay, basic magnesium carbonate, zinc oxide, certain blacks, antimony pentasulfide, iron oxide, titanium oxide, zinc sulfide, and a series of organic dyes. Common to all these pigments is the fact that they consist not only of particles with sharply outlined contours, but also generally of a "granular" fraction, the particles in which are either colloidal or nearly colloidal in size. (It is not surprising that uniformity in the degree of subdivision of a pigment is not obtained by the commercial methods of manufacture used.)

An attempt has already been made to set up a system of classification which would distinguish between active and inactive pigments on the basis of the proportion of colloidal matter present. In the case of carbon blacks, this differentiation is based on the striking fact that vulcanizates containing a pigment such as inactive "Thermax" (thermatomic carbon) are the only ones showing well-defined particles of carbon (Fig. 27, page 667), whereas those containing active (reinforcing) channel black in the same concentra-

* Translator's Note. Since the author of this section has placed the pulverized minerals in a separate class (discussed above), the word "pigment" is here used by the translators in a slightly more restricted sense than that covered by the definition on page 374.—V. N. M.

tion show no particles resolvable even at high magnification. With the channel black stocks, the microscope reveals only a fine "granulation" (Fig. 24, Plate VI), such as is to be expected from a dense dispersion of colloidal particles. Between these two extremes are numerous carbon blacks (representing transition stages) which seem to show both "active" (reinforcing) and "inactive" properties in rubber stocks, and which are found microscopically to contain both well-defined, non-colloidal particles and colloidal particles which cannot be resolved. In microscopic evaluations, it is therefore better to distinguish between active and inactive particles or particle fractions rather than between active and inactive kinds of compounding ingredients, since the "transition" pigments or pigment mixtures found in the majority of vulcanizates are more readily characterized by the former system. Consequently the first interest of the microscopist lies in the determination of the relative proportions of colloidal (active) and non-colloidal (inactive) particles present in a specimen, and it is only in particular cases that an estimate of the absolute particle size has to be made.

The problem is not such a simple one with all pigments. For example, the optical properties of basic magnesium carbonate and of kaolin are so similar to those of rubber that, even in concentrated mixtures, only the coarsest particles can be recognized. On the other hand, carbon black, zinc oxide, antimony pentasulfide and certain dyestuffs (which can be finely dispersed) make themselves evident in rubber stocks, even though they are in the colloidal state. Their capacity for accomplishing this result is to be attributed to their high index of refraction and good reflecting power.

Although basic magnesium carbonate and kaolin may be incorporated (by suitable processing) in stocks which remain practically transparent, the same is not true for the active fractions of carbon black, etc. Even with the most careful processing, these latter do not lose their covering power, except with respect to the longer wave lengths of the visible spectrum (and with them only partially). It is observed that with rubber mixes containing submicroscopic carbon black, zinc oxide, or antimony pentasulfide, there is a microscopic transparency of the thin sections to reddish-yellow light, which is characteristic of colloidal dispersions of these materials in other media. No particular magnification is required for the detection of these pigments in rubber. With the above-mentioned "transition" pigments, which do not contain colloidal particles exclusively, or with prepared mixtures of active and inactive pigments, it is observed that the transparency to reddish-yellow light exists, although it is more or less concealed by a gray color. In such a case, it is necessary for the microscopist to use a higher magnification to determine whether he is dealing with a uniform kind of pigment or a prepared mixture. Examples of these two possibilities are shown in Figure 25, Plate VI and in Figs. 8 and 9, Plate III respectively. Only in the limiting case of the so-called "inactive" pigments is the color clear and the general appearance unequivocal. The color of rubber containing one of these materials is usually almost a pure gray, since the optically resolvable particles present exhibit a certain covering power with respect to the visible field as a whole. This "neutral gray" is also to be observed in the case of the examination (at low magnification) of stocks containing such colored pigments as iron oxide or antimony pentasulfide, provided the diaphragm of the substage condenser is not opened too far.

When it is a matter of finding a very small proportion of reddish-yellow

to brown in the transmitted light (that is, when dealing with compounding ingredients which are estimated to contain not over 5 per cent of "active" particles), it is necessary to exceed the usual concentration of the pigment in the mix (which is generally 1 or 2 per cent) somewhat and to cut down the thickness of the section proportionately. This necessity is especially evident when a sensitive comparison of materials is being attempted. As far as the microscopic analysis of commercial vulcanized products is concerned, very favorable conditions usually prevail, since those pigments which have a low content of submicroscopic particles must be used in high concentration in order to obtain any appreciable "activation" (reinforcement) of the rubber. In case the concentration of such pigments is so low that a satisfactory determination of the proportion of colloidal particles is not possible by means of the light transmitted, the microscopist is generally spared the trouble of attempting a determination, since the colloidal particles at such a great dilution no longer exert a specific influence of any practical significance.

Examples of the transmitted colors characteristic of the various kinds of zinc oxide, carbon black, and antimony pentasulfide commonly encountered during the examination of manufactured products have been assembled in Figure 28. These colors have been reproduced directly from thin sections of the original mixtures of pigment and rubber. Since the color tone has been found to be somewhat dependent on the size of the opening in the diaphragm through which the light passes, a uniform adjustment of the diaphragm was maintained throughout the work on the comparison of transmitted colors. (*See* p. 667.)

The first series of pictures in Figure 28 shows the absorption colors of different kinds of zinc oxide. The nearly gray color of the third reproduction is especially easy to detect. This color is found for instance with the "Horse Head" brand of American zinc oxide and of various grades of zinc gray and zinc white, the average particle size of which has been increased by reheating subsequent to original manufacture. As has been mentioned by Green,[17] the color of the light transmitted by a mix of this kind, when examined under high magnification, corresponds to that characteristic of well-shaped individual particles of known crystalline form. Since it has been established that the domestic (German) brands of zinc oxide have crystalline forms which are less well defined, the detection of the various grades of zinc oxide of American origin is not very difficult. If the microscopic studies are extended to include the use of ultra-violet light, it is observed that thin sections containing the American types of oxide can be easily distinguished from those containing domestic brands as a consequence of the fact that the former contain no particles which exhibit a blue-green fluorescence.*

A reproduction of a mix containing a well-known domestic "Red Seal (Rotsiegel)" zinc oxide is presented in the second picture (Figure 28). A considerable content of colloidal particles, which transmit red and yellow light, is evident. The more expensive "Green Seal" or "White Seal" grades do not appear to give microscopic pictures differing essentially from that shown for the "Red Seal" product. Since both reddish-yellow and gray

[17] *J. Franklin Inst.*, **192**, 637 (1921).

* Translator's Note. At the present time there are so many types of zinc oxide of American manufacture that these generalizations would scarcely be expected to hold strictly.

The microscopic study of pigments using ultra-violet light has been discussed recently by G. S. Haslam and C. F. Hall [*J. Franklin Inst.*, **209**, 777 (1930); *J. Optical Soc. Am.*, **24**, 14 (1934)]. The advantages to be gained by the use of ultra-violet photomicrography in the determination of the average size of pigment particles which approach the limit of resolution of the ordinary microscope are described by these investigators, as are also the results of studies of pigment mixtures and co-precipitated pigments.—V. N. M.

colors are evident in the transmitted light, it is not surprising that a relatively large number of well-defined particles are also to be observed during examination under high magnification.

"Kadox" zinc oxide (pictured in Field 1), as well as certain similar German grades manufactured in Hamburg, gives a clear picture showing the much more intensive reddish-yellow coloration which is indicative of a high content of colloidal particles. Microscopic examination shows an almost complete absence of resolvable particles, especially in the case of "Kadox." There is to be observed a "granulation" of reddish-yellow color, which can be differentiated only with the ultramicroscope. (*See* "Investigations in the Dark Field"; p. 672, Fig. 213, Type III.)

When desired, relatively exact determinations of the type of zinc oxide present in a highly concentrated mix can be made on the basis of the characteristics discussed above. A thin section of a known mix of approximately the same concentration is used for comparison. Both samples are brought to the same thickness by pressing them in the plate glass press. It is then possible to establish whether the zinc oxides used are of the same type or whether they are of different particle size. The case in which the results are rendered doubtful as a consequence of the use of a mixture of oxides of different degrees of fineness is seldom encountered.

The second series (Fields 4 to 6, Figure 28) shows the transmitted colors characteristic of different kinds of carbon black which are frequently to be found in products of European manufacture. These reproductions were made under low magnification and under the same conditions as those of the stocks containing zinc oxide. The results of microscopic investigations of these mixes, together with that of one containing thermatomic carbon, are shown in Figures 24, 25, 26, and 27, Plate VI.

In Field 6 is shown an example of a heavy lampblack, the transmitted color of which approaches but does not entirely correspond to a neutral gray. In sufficiently concentrated mixtures, the color is found to have a reddish tinge. Microscopic examination of such mixtures reveals sharply defined particles of characteristic growth forms (dendritic). (*See* Fig. 26, Plate VI.) The nature of the formations observed has often led to the conclusion that coagulation occurs during vulcanization. The size of these particles is about the same as that of a normal zinc oxide, such as the "Red Seal" brand. This similarity in size is evident from Figure 9, Plate III, in which the two pigments are shown together. Comparison of several lampblacks manufactured by different companies shows that there are many different types, which may be distinguished on the basis of color tone, and furthermore that the size of the well-defined particles varies considerably within the product from any one plant. For example, the "Durex" grade of commercial black contains numerous particles which are spherical in shape and relatively fewer of the usual coarse particles with shapes characteristic of crystalline growth. Nevertheless, the transmitted color in the case of a black of this type is not strikingly different from that usual with lampblacks.[18]

A more bluish-gray transmitted color is indicative of "Thermax" (thermatomic carbon) rather than lampblack. The investigation of mixes containing "Thermax," even with the ultramicroscope, fails to reveal "active" particles, but shows instead clearly visible spherical particles. On the basis of these

[18] The relatively small proportion of colloidal particles which influence the transmitted color of this type of lampblack cannot be observed at all with bright field illumination. If necessary, these finer particles can be detected in the dark field, owing to the fact that they scatter blue light.

observations, it is easy to distinguish thermatomic carbon particles from the irregularly shaped lampblack particles of the same average size. (Fig. 27, Plate VI.)

The best grades of domestic (German) lampblack, in contrast to those discussed above, show a transmitted color of medium shade, as is illustrated in the fifth picture of Figure 28. In highly concentrated mixtures with rubber, such a black exhibits a color tone which is distinctly reddish. Under the microscope, there is evident a very fine "granulation" which cannot be entirely resolved, even at high magnifications. Only a few black particles of the same size and shape as those present in heavy grades of lampblack are to be seen. To distinguish these two classes of lampblacks microscopically is of interest, since 25 per cent of the better class in a rubber stock shows an "activating" (reinforcing) effect, whereas at least 40 per cent of the heavier grades is required to give a similar effect.

In the fourth field is reproduced the reddish-brown transmitted color exhibited by stocks containing reinforcing American gas black in the same concentration as that of the lampblack stocks just discussed. The picture obtained with gas black possesses a clearness resembling that characteristic of "Kadox." Even at the highest magnification clearly defined gas black particles cannot be seen. (Fig. 24, Plate VI.) The only particles visible (and these are also to be seen in the so-called "aerfloted" black) are isolated, round, graphitic particles, which always accompany gas blacks and which are of the same order of size as inactive thermatomic carbon. (Fig. 7, Plate III.) Characteristic deviations in the transmitted color of gas blacks as a consequence of variations in the number of graphitic particles present are seldom encountered in vulcanized rubber goods. Although blacks showing transmitted colors which deviate from each other for this reason do exist, they are seldom used in the rubber industry. An explanation of the typical differences in the effects on the physical properties of stocks produced by different gas blacks can often be obtained by the use of the microscope. Thus the differences in the effects produced by "Arrow 4" and "Arrow 6" blacks can be attributed to the fact (observed microscopically) that the former has a higher degree of fineness.

As a rule, it has been found that American products containing gas black (tire treads, for instance) are more easily analyzed than those of European origin. In most American stocks, zinc oxide and undispersed black are to be seen, as is also thermatomic carbon in the cheaper products. Combinations of this type readily lend themselves to microscopic analysis. Types of carbon black having about the same degree of fineness as lampblack (Gastex and Flex-black, for example), which have been recently developed in several forms, do not yet seem to have been adopted by the industry to any great extent. In contrast to American products, those manufactured in Europe contain not only all kinds of lampblack, but also mixtures of such with gas black. These mixtures are not easy to evaluate microscopically, and the estimation of their technical effects in rubber is difficult.

Three samples taken from the treads of well-known tires (manufactured in 1927 or 1928) are shown in Figures 7, 8 and 9, page 649. Figure 6 shows the appearance of gas black (in an American tread stock) at a magnification of about 800×, when nothing else is present save scattered particles of zinc oxide not seen in the section shown. In the English stock shown in Figure 7, it is evident that a small amount of lampblack has been used with the gas black. A much higher proportion of lampblack, together with some zinc

oxide of about the same particle size, is apparent in the French stock (Fig. 9). In addition, certain European treads contain two layers, the lower and larger of which contains lampblack and zinc oxide. The thinner upper layer (veneer) consists of a gas black stock. (*See* English products shown in Fig. 21, page 666.) Typical solid tires seem to contain lampblack with very little gas black (Figure 9, Plate III) or lampblack alone (Figure 22, Plate V).[19]

Exact determinations of the identity and degree of fineness of lampblacks are best made when one or more mixes containing known lampblacks are available for comparison. A small amount of gas black in the presence of lampblack can only be determined with certainty in the dark field. (*See* "Investigations in the Dark Field," p. 675.) No trouble is caused by any zinc oxide present, since this pigment is usually present in small quantity, and it dissolves after a time in the Canada balsam in which the preparation is embedded.

The third series (Fields 7 to 9, Figure 28) illustrates the transmitted colors characteristic of various grades of golden antimony (pentasulfide), which are frequently found during analysis. In the case of the antimony sulfides (tri- and penta-), there exists no such simple relationship between particle size and transmitted color as is found with zinc oxides and blacks. In fact, the various trisulfides show both variegated and pure transmitted colors, whereas in the case of the pentasulfide the colors are red to yellow.

When a pure transmitted color is obtained with antimony trisulfide, it is found that the sample being examined is characterized by great uniformity in particle size. Variegated colors are seldom obtained with technical vulcanizates, since such colors are characteristic of a type of trisulfide which is not used to any great extent. The most common deep red and bright red grades yield a tinted gray color, which is easy to identify, and which indicates that the particles are not colloidal. The gray color may be tinted weakly blue-violet, red-violet or blue-green (varying with the method of preparation and with the transparency of the particular sample of pigment). Under the microscope the particles are all visible and well-defined, as are those of "inactive" blacks. No particles which scatter blue light are revealed by the ultramicroscope.[20] Particles of colloidal size occur only in the grades which give transmitted colors of almost pure yellow, resembling those obtained with the antimony pentasulfides.

On the other hand, submicroscopic particles are found in all types of pentasulfides, three of which were used in obtaining pictures 7 to 9 (Figure 28). The transmitted colors shown approach those of the finer zinc oxides and the gas blacks. The results of color photography thus confirm the experience of rubber compounders who include golden antimony among the pigments having some reinforcing power. The especially fine grades (precipitated with 50 per cent of sulfur) give a transmitted color which is a very bright yellow (Field 7), whereas the slightly coarser grades (17 to 20 per cent of sulfur) and the so-called pure grade (6 to 10 per cent of sulfur) yield a solid orange-yellow (Field 8). Even at the highest magnification with the microscope, no clearly visible particles are evident, except for grit particles which cannot be dispersed and which seem to be unavoidable in the method of manufacture used. Figure 15, Plate V is illustrative of a

[19] For the past several years solid tires have also been manufactured with a veneer or relatively thin upper layer consisting of a highly reinforced (gas black) stock, which resists abrasion much better than does the stock comprising the main body of the tire.—V. N. M.

[20] See Pohle, *Kolloid-Z.*, **39**, 1 (1926).

mix containing antimony pentasulfide of the type pictured in Field 8, Figure 28.

Types of pentasulfide of high coloring power, which have thus far not been produced in Germany, are capable of giving a transmitted color which represents a transition stage between those of the trisulfides and those of the usual pentasulfides. Such grades are to be observed in products of French or American origin. The transmitted color (Field 9), which is a somewhat cloudy, dull red, indicates that a mixture of particles of various sizes is present. Microscopic examination reveals both well-defined particles and finer, unresolvable ones. The latter are evidently not of such a size as to permit of an orange color, as there is no evidence of orange or yellow in the color obtained. The degree of fineness seems to be about the same as that of the finer lampblacks. The differences between pigments of this type can be better revealed by dark field examination (*see* p. 674). In the literature [21] are to be found the results of analyses of antimony sulfides of English, French, and German origin.

Specimens for the study of various grades of antimony sulfides can be obtained from automobile inner tubes of older manufacture and also from gas tubing, rings for sealing bottles and jars, and surgical articles. These products, which at times contain both pentasulfide and trisulfide, cannot be evaluated completely except at high magnification. Characteristic microscopic pictures can also be obtained from the cheaper grades of red vulcanizates which contain ground vulcanized scrap. Any pieces containing antimony pentasulfide stand out in such stocks because of their reddish-yellow color, which can be distinguished in a matrix colored with the trisulfide.

Dispersion series corresponding to those shown in Figure 28 can be prepared in the cases of various iron oxides, dyes, or other pigments. However, the practical importance of such studies is not very great, since these compounding ingredients are not ordinarily incorporated in rubber stocks in quantities sufficient to affect the properties of the latter to any extent. Great familiarity with the degree of fineness of such pigments is not generally necessary, when the problem is one of evaluating a vulcanizate of unknown composition. The shades of color of these pigments themselves provide the simplest criterion of their value. Titanium oxide constitutes the only certain exception to this statement. The occurrence of a pure (bluish) white color, which is characteristic of many grades of titanium oxide, is closely related to the degree of dispersion of the pigment in rubber, and makes justifiable a subsequent examination of the stock.

Investigations in the Dark Field

Although examination in the dark field is often desirable as a control for bright field examination, it is seldom feasible, since the sensitive optical equipment used puts severe requirements on the nature of the preparation. The arrangement of Siedentopf, which consists of a powerful ultra-condenser in combination with a highly concentrated source of light, is recommended for investigations of this type. The procedure for such an examination is the same as that of the bright field examination of a thin section or layer which has been brought into the focal point of the condenser. It has been found that the concentration of pigments in the rubber product to be examined is not a matter of great importance with this method, but that (in

[21] Shirk and Wilson, *India Rubber World*, **66**, 612 (1922).

Fig. 10. Radial section through the carcass of an older Goodyear tire. Individual cords cut perpendicularly and held together with dark brown rubber compound. Alizarin coloration of stock between plies made possible by accelerator present. (Cf. p. 653.) Thin section. Zeiss apochromat, 16 mm.

Fig. 11. Breaker fabric, imbedded in a pigment-free layer of latex (older Goodyear construction). Fiber below; rubberizing compound above. (Cf. p. 653.) Thin section. Leitz—1/7.

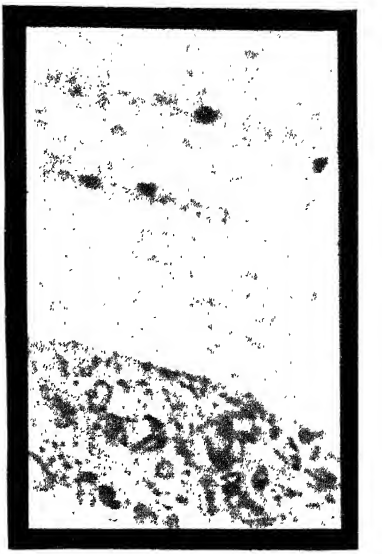
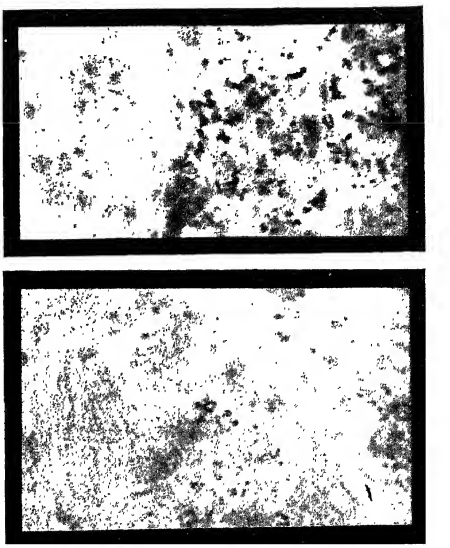


Fig. 12. Coloration of magnesium carbonate and lime with alizarin in an unvulcanized stock. Sulfur and litharge also present. (Cf. pages 654 and 656.) Thin section. Zeiss apochromat, 16 mm.



Figures 13 and 14. Latex vulcanizates exhibiting irregular dispersion of zinc oxide, lampblack, and kaolin (grit with fan-shaped structure), prepared by means of the older Anode process. (Cf. pages 647 and 656.) Thin section. Leitz—1/7.

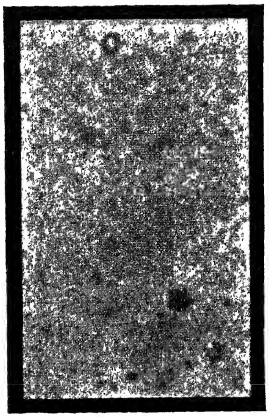


Fig. 15. About 20% of antimony pentasulfide (predominantly submicroscopic).

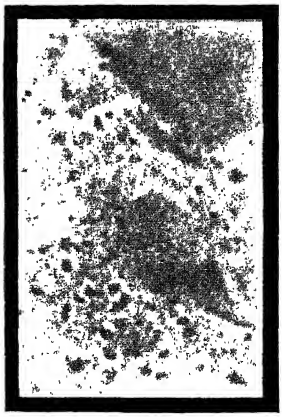


Fig. 16. 5% of zinc oxide and pieces of brown factice (oil substitute).

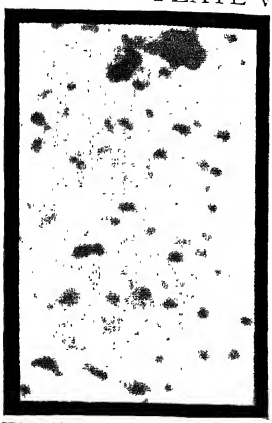


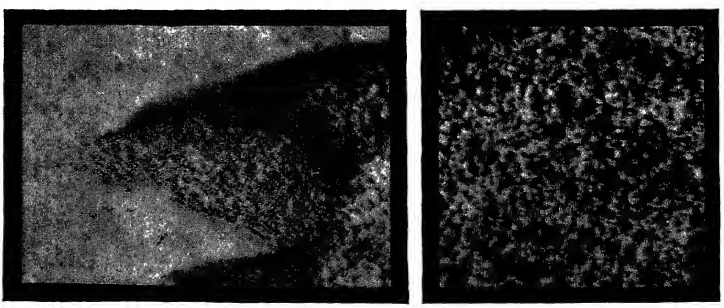
Fig. 17. 4% of relatively coarse antimony trisulfide.

Fig. 18. About 10% of antimony sulfide and some pulverized mineral (chalk).

Fig. 19. Organic dyestuff, partly dissolved (bright yellow) and partly crystallized out. Zinc oxide also present.

Fig. 20. Zinx oxide, pieces of factice, and magnesia (stained with alizarin).

Figures 15 to 20. Various compounding ingredients in inner tube stocks with high rubber content (after normal processing). (Cf. pages 647, 654, and 663.) Thin section. Zeiss apochromat, 2 mm.



Figures 21 and 22. Normally processed black stocks containing a high proportion of pigment. Tread stock with colored "granulation" due to gas black, and adjoining base stock with coarser lampblack (21). Solid tire stock containing lampblack but no gas black (22). (Cf. pages 658 and 663.) Thin section. Leitz—1/7.

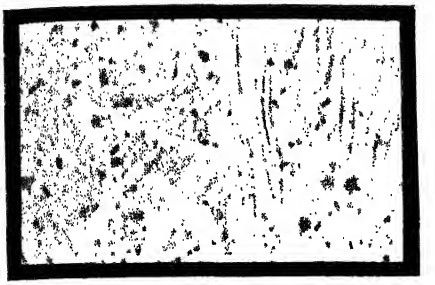


Fig. 23. Rubberizing compound near the cord (partly stained with alizarin). Insoluble pieces of mineral rubber visible. (Cf. pages 653 and 655.) Thin section. Leitz—1/7.

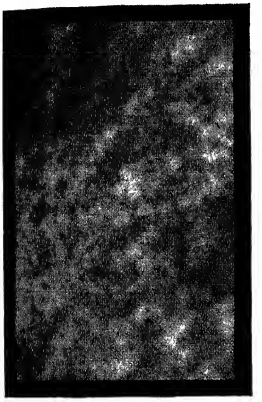


Fig. 24. Submicroscopic gas black "granulation."

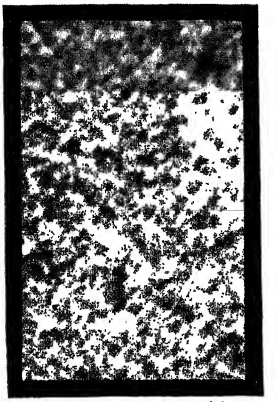


Fig. 25. Fine grade of lampblack (partly submicroscopic), exhibiting coarser "granulation."

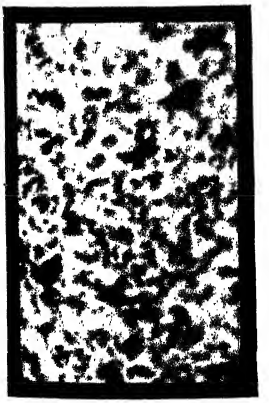


Fig. 26. Heavy lampblack.

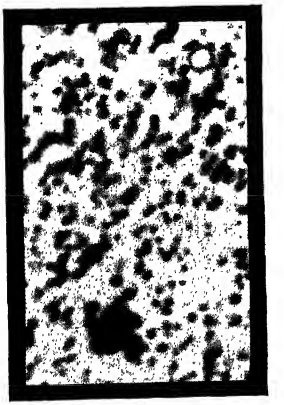


Fig. 27. Thermax.

Figures 24 to 27. Typical appearance of stocks containing about 40% of common blacks. (Cf. p. 661.) Thin sections. Zeiss, 2 mm.

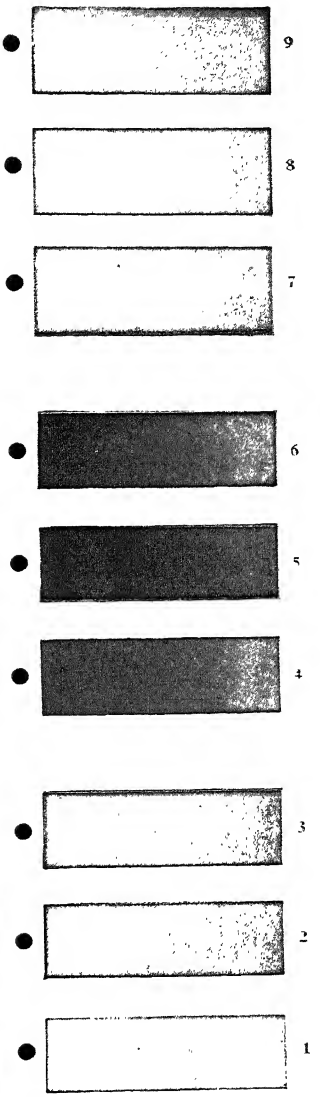


Fig. 28. Transmitted colors of various finely dispersed pigments. Zinc oxides (1 to 3). Blacks (4 to 6). Antimony pentasulfides (7 to 9). (Cf. pages 660 to 664.) Reproduced from original layer. Natural size.

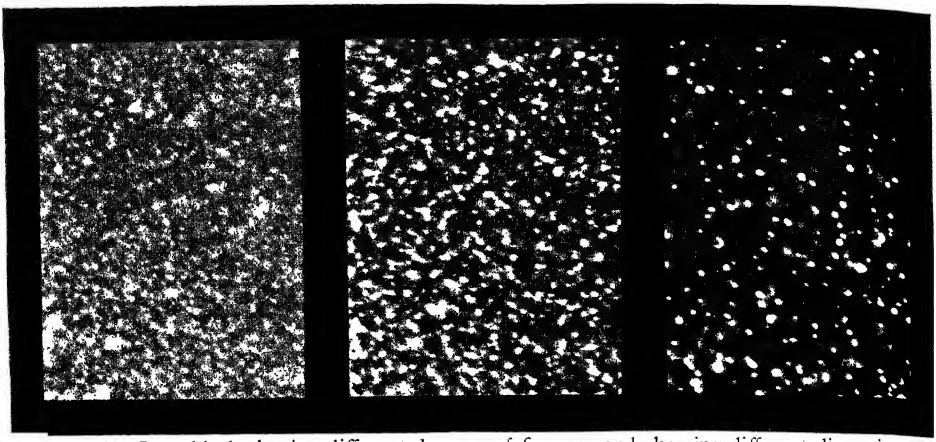


Fig. 29. Lampblacks having different degrees of fineness and showing different dispersion colors (about 1% concentration in the rubber). (Cf. p. 674.) Thin section. Leitz—1/7.

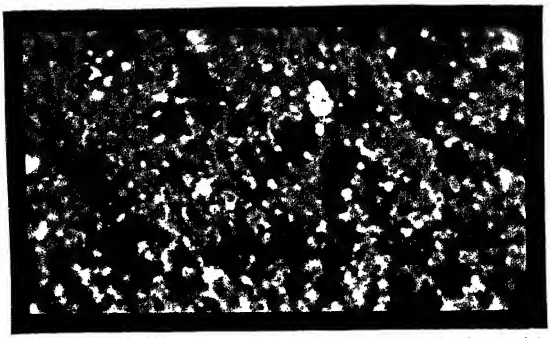
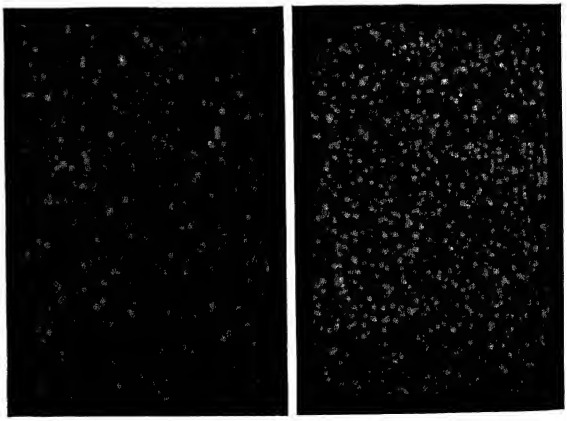


Fig. 30. Solid tire stock, containing zinc oxide and lampblack, but without a perceptible content of submicroscopic particles. (Cf. p. 675.) Thin section. Leitz—1/12.

Fig. 31. Luminescence in the dark field (transparent vulcanizate). (Cf. p. 670.) Thin section. Dark field diaphragm. Zeiss apochromat, 16 mm.



Figures 32 and 33. Inner tube stocks, containing a fine (left) and a somewhat coarser grade (right) of golden antimony. (Cf. p. 674.) Thin section. Leitz—1/7.

contrast to bright field examination) consideration must always be given both to cloudy and to bright spots in the rubber substance itself. Such spots constitute a significant source of error in the study of fine and weakly reflective pigments in rubber. It is therefore advisable not to use dark field microscopy as a quantitative method of analyzing stocks of low pigment content, but rather to limit it to qualitative estimations based on the use of comparison preparations.

Certain results obtained with technical stocks, in which the pigments were in part colloidally dispersed, are discussed below. From these it can be seen that estimations of practical importance can be made from general (large field) pictures which are not of such a nature as to permit of numerical determinations.

For a quantitative evaluation (with respect to a standard sample), employing the well-known methods of ultramicroscopy, an especially favorable example, such as that of the various grades of zinc oxide, is necessary. This process is usable with only a few pigments, which reflect light unusually well and which consist of well-defined particles.

The dark field phenomena in the rubber substance itself, and the causes therefor, are only partially understood, since the standard necessary for satisfactory comparison—optically clear rubber—has never yet been prepared. As far as can be learned from the study of pure gum vulcanized samples, it seems that the bright spots observed arise partly from Tyndall phenomena and partly from luminescence phenomena. In addition to cloudy inhomogeneities, there are often bright radiations, which are to be distinguished on the basis of color and intensity from the similar effects produced by the fluorescing of dissolved compounding ingredients. Provided no added materials are present to obscure the phenomena, these spots are microscopically visible with ultra-violet light, a bright bluish-green fluorescence being evident. This fluorescence constitutes a source of error in connection with luminescence analysis which has heretofore not been given consideration. (For a discussion of recent investigations of the fluorescence of rubber and rubber pigments, *see* page 642.)

In very transparent rubber goods, it has been found that the intensity of fluorescence of the rubber substance is influenced by the sulfur content, by the accelerator content, and by the degree of heating. Accordingly, it may be concluded that an irregular distribution of intensity in the microscopic field of view is the result of irregular vulcanization or irregular distribution of the vulcanizing ingredients. Moreover, microscopically large zones of overvulcanization, such as parts of the carcass of a tire which had developed a high temperature while running, can be recognized as a consequence of the accompanying bright radiation. (*Also see* p. 645.) Such bright zones in stocks of low pigment content are especially disturbing, since, during their examination in the dark field, all of the section illuminated by the condenser emits radiation. As a result, it is generally necessary in such work to use a colorless filter of quinine sulfate (as an acidified solution in a 1 cm. bulb), which absorbs the exciting radiation. Conversely, dark field investigation of the microscopic distribution of intensity is best carried out with visible light excluded. The simplest method of removing the visible light is to make use of an ultra-violet "black" glass filter (perhaps supplemented by a copper sulfate filter, consisting of a concentrated solution in a 3 cm. bulb) in front of the source of light. The copper sulfate filter is only necessary when it is

desired to keep out all of the red light. The extreme red not absorbed by the ultra-violet filter glass is frequently not undesirable, since by means of it the investigator can obtain a picture of the non-luminescing details in bluish red. The connection between the luminescing and non-luminescing elements can thus be established.

The simplest determinations of this kind can be made without the use of a special quartz condenser. They require, of course, a frequent re-focusing of the condenser in the vertical axis and the use of a very thin slide in order to get the condenser as near as possible to the preparation. In case the very fine focus of the ultracondenser does not suffice for the illumination of the larger points of interest in the preparation, it is necessary to resort to less concentrated light at lower magnification (about 150×). Such light can be furnished by placing a round central stop of about 15 mm. diameter in the ordinary bright field condenser. Figure 31, Plate VII, illustrates the appearance of a so-called transparent vulcanizate in the ultra-violet dark field, when examined after definite precautions have been taken.[22] Along with the uniformly distributed luminescence, there are some radiating zinc oxide particles, which usually can be seen in "transparent" products. The fine-grained "granulation" of the background, which is visible during subjective observation, does not appear on the plates.

In contrast to these radiation phenomena, the peculiar Tyndall phenomena within the rubber substance itself are not so easy to eliminate, since they are probably dependent on the fact that the rubber and other raw materials are only "technically" and not absolutely pure. They cannot be avoided by any possible variation of conditions, although they do seem to be definitely influenced by the degree of working of the rubber on the mill. Thus laboratory mixtures which are masticated slowly and repeatedly contain many cloudy particles, whereas those which are worked less intensively show a much clearer rubber substance. Longer milling on close rolls seems to favor the collection of dust from the atmosphere and the removal of finely divided material from the surface of the roll, which latter material frequently leads to a visible coloration in clear grades of crepe rubber. In thin sections, the vulcanized rubber generally shows a finely granulated appearance, as well as dust particles of various sizes. It is not necessary to attempt to identify these latter particles. In comparison with the appearance of added pigment particles, the blue color of the "granular" field is less noticeable and is characteristic. In the most favorable cases this blue color can be distinguished, owing to contrast with the general brightness. This contrast can be brought out in photography by the correct choice of exposure. (*See* p. 672.)

There is, however, no evidence of fine structures or primary particles in the rubber substance, since the treatment of the sample with the usual swelling agents precludes the formation of structural elements which are optically very closely related to the rubber itself. Moreover, individual latex particles are not visible in vulcanized products made from latex. Furthermore, the finely dispersed impurities, which are often found to give a cloudiness in crude rubber, and which also become apparent in vulcanizates after treatment with water, ether, etc., become lost without leaving a trace in the case of the normal preparation made in the presence of swelling agents.

As in the case of investigations in the bright field, standard preparations, which reveal the characteristic appearance of the most important pigments,

[22] See Pohle, *Z. wiss. Mikroskop.*, **44**, 183 (1927).

are used for comparison in dark field examinations. To be sure, dark field observations necessitate rather strict requirements with respect to the concentration and the thickness of the sample, since it is obviously impossible to focus on a single optical section of the preparation when all particles lying in the path of the beam of light but not in the focus also become luminous. Moreover, comparison slides should contain a layer of pigment-free rubber, which has been masticated in the same manner as the samples being studied, and which provides a control as far as the experimental conditions and the rubber itself are concerned.

Preliminary tests are necessary to determine the concentrations which will permit of sufficiently distinct images of the pigments in rubber. These concentrations are primarily dependent on the degree of fineness of the particles. With the so-called "active" pigments, these most desirable concentrations are found to be outside the range used in technical products. In order to obtain layers of suitable thickness, it is advantageous to prepare wedge-shaped specimens (when possible, by the use of two plane parallel, ground glass plates). For this purpose, a sample of the stock is placed along the edge of the cover glass (which later forms the edge of the wedge of rubber stock), is warmed to about 60° C., and is then exposed to pressure in the

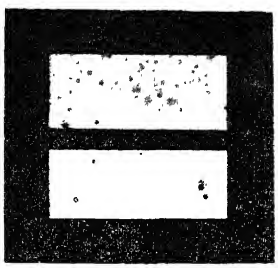


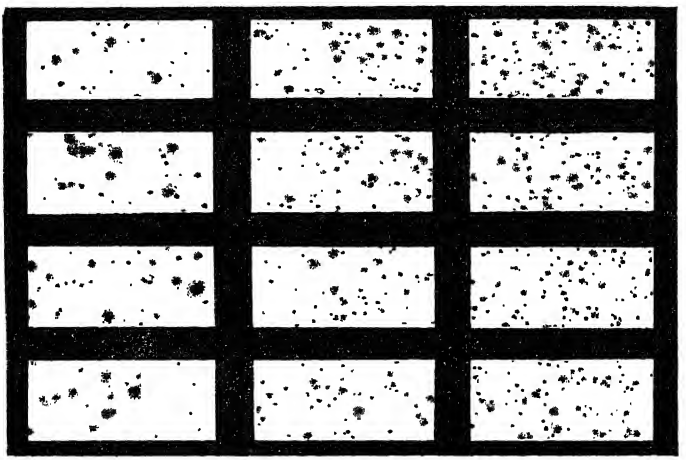
Figure 212—
Rubber, masticated without the addition of pigments.

plate glass press. The pressure is applied at one end of the press only, the section thus being given the shape of a wedge. The portion suitable for examination is near the middle of the preparation, since the ends have a decidedly uneven slope. The boundary line between the two parts of the comparison preparation should be as level as possible. The parallel displacement of the preparation along the edge is best accomplished by means of a mechanical stage, after the edge has been arranged parallel to one axis of the stage.

In the few cases in which these preparative and optical requirements can be fulfilled, the images obtained are quite useful, as they are suitable for the photographic recording of the number of particles present in a mix containing a given quantity of a pigment. Figure 213 shows mixes containing various grades of zinc oxide at a low particle density and exposed to light of strong intensity. The masticated rubber used as a control is shown in Figure 212. The comparison wedge-shaped layer is composed of narrow sections of the three mixes with a section of the pigment-free rubber at each end of the wedge. The uniformity of thickness of the layer along the edge of the wedge can be tested by comparing several successive fields in each section with respect to particle density. If the layer is uniform in thickness, there should obviously be no change in the apparent distribution of particles as the observer moves from one side of the section to the other. The comparison between samples is made by taking a series of pictures of each mix

in the comparison wedge. Four of the negatives from each of these series are chosen for printing. Two separate exposures of the pigment-free rubber in the comparison preparation are also taken.

For subjective observations, the dark field is first standardized against the pigment-free section of the preparation. This step in the procedure, which is made on a portion of the section as near as possible to the boundary line between sections, reveals the fine, turbid, granulated appearance of the rubber substance, as well as a few coarse dust particles embedded in the rubber. (*See* Fig. 212; sample exposed 40 seconds.) The parallel displacement of the preparation, so as to bring the first of the sections containing zinc oxide into the field of view, is best done by means of the mechanical stage. In this section (Type I of Fig. 213) are to be seen brightly shining particles which illuminate the granular-appearing background to some extent. In the other sections (Types II and III) the particles become progressively finer and more frequent. In fact, some of them are difficult to distinguish clearly from the "granular" background. By introducing a flat disk under



Type I Type II Type III

Figure 213—Rubber, masticated with the addition of zinc oxide (0.025%) of different degrees of fineness. Leitz plate condenser; oil immersion, 1/12.

the condenser, or by reducing the light by means of the diaphragm in the objective, it is possible to cut out the "granulation" in these fields during subjective observations. As already mentioned, the same thing can be accomplished when taking photographs by a proper choice of the time of exposure. While an exposure of 30 to 40 seconds is required to bring out the turbidity in the rubber substance, only about 15 seconds is required for photographing the particles of zinc oxide. An average period of 25 seconds does not reveal any appreciable number of additional zinc oxide particles and at the same time does not permit the "granulation" to show. The intensity of the light from the zinc oxide particles is so much greater than that from the "granulation" of the rubber substance that any significant tendency to confuse the two is absent. Dust particles, which could constitute a source of error, can be counted in a series of photographs of the pigment-free rubber, and their number deducted from the total number of particles present. The

average number of such particles per field in the preparation shown in Figure 212 (25-second exposure) is 4.5, which is not sufficiently large to exert much of an influence on the relative values obtained for the three grades of zinc oxide.

An equally satisfactory picture is possible in the dark field in the cases of pigments with particles similar in size to those of zinc oxide. Included among such pigments are red iron oxide, antimony trisulfide, zinc sulfide (lithopone), and the heavy lampblacks. This group comprises essentially the pigments which have high covering power, and the particles of which consequently have a decided capacity for scattering light. Information regarding these bright particles is also obtained from their colors in the case of subjective observation. With the finer grades of lampblack and golden antimony, the accuracy of the observations in the dark field decreases as the particle density increases and as the relative luminosity of the field with respect to that of the standard mix decreases. Thin sections and low concentrations of pigments in the mixes are requisites for satisfactory observations.

There is no quantitative method based on the determination of the degree of fineness with dark field illumination in the cases of channel black, precipitated zinc oxide, and other pigments having similar particle size.* The phenomena in the case of fine particles of such pigments do not contrast sharply enough with the phenomena exhibited by the rubber itself. Moreover, the finest fractions cannot be resolved by the microscope. The dark field picture of mixes containing reinforcing pigments is thus similar to that obtained in the bright field in that it also has a granular appearance. Furthermore, the particle density cannot be easily observed, even when the concentration of the pigment in the mix is reduced to less than one part in a thousand. Decreasing the thickness of the section to the lowest possible value results in little improvement and increases the possibility of unevenness in thickness, since the layers tend to form vacuoles when pressed out too thin.

The evaluation of such dense preparations as those just discussed must therefore be accomplished by other methods, the best of which involves the investigation of turbidity and color phenomena in a larger field under a lower magnification. The phenomena which come into consideration in such evaluations are related to and in a sense complementary to those of the transmitted colors which were previously discussed in connection with mixes of pigments and rubber. By partially closing the iris diaphragm in the objective, it is possible to make the color of the field of view and of the individual particles more or less apparent and thereby improve the characteristics of the dark field image. For comparison, it is also necessary to have a standard preparation of the same thickness, which can be illuminated in the same field as that containing the mix being studied. This requirement can be readily fulfilled, in the case of thin sections of vulcanizates of low pigment content, by embedding the two parts of the comparison preparation in Canada balsam under the same cover glass and compressing and fixing the layers in the manner previously described. (*See* p. 648.) Examples of the types of compounds which lend themselves to study by this method include different kinds of inner tube stocks, lightly compounded carcass stocks, and sometimes

* Translator's Note. By dispersing such a pigment as channel black or zinc oxide in rubber on a mill and then dissolving the stock in a solvent, S. D. Gehman and T. C. Morris [*Ind. Eng. Chem., Anal. Ed.*, **4**, 157 (1932)] have obtained a solution suitable for the determination of the particle size of the pigment involved. A Zeiss cardioid ultramicroscope was employed in this work.—V. N. M.

compounds of the solid tire type. Decidedly undervulcanized samples, which are the most easily deformable, are preferred for these preparations.

Dark field comparisons, carried out in the manner described above, yield the same series (varying with the proportion of the total light scattered) with the individual pigments as are also obtainable on the basis of the transmitted colors. Dark field comparison, which is applicable to finer fractions among the individual pigments than is the bright field, overlooks more easily the smaller particles of grit which stand out prominently in the bright field.

In general a red-brown color in the bright field corresponds to an intensive blue-violet color in the dark field. Thus the three types of zinc oxide shown in Fields 1, 2 and 3 of Figure 28 can be distinguished just as well by the proportion of blue in the diffracted light or by the relative number of blue-violet particles when the size of the opening in the diaphragm has been sufficiently reduced. The same is also true for other series of pigments, such as the various blacks pictured in Fig. 29, page 668. In this figure are shown sections of gray-colored vulcanizates, containing the same quantity of zinc oxide and various domestic grades of lampblack. The two blacks in the outermost fields of Figure 29 have already been shown in Figures 25 and 26 of Plate VI and Fields 5 and 6 of Figure 28. After the zinc oxide dissolves (which it usually does very soon after the section is embedded in Canada balsam), the dark field images characteristic of the various blacks become evident, and the sequence from Field 1 to Field 3 can be recognized.

The dark field images confirm the information obtained from practical experience; that is, that colors which are often not of the same bluish-gray tone are obtained with blacks having different degrees of fineness. The difference arises from the fact that the scattering of blue-violet light by the individual particles of the finer types is considerable. As a consequence, the color by reflected light is not a neutral bluish gray. The finest lampblacks yield greenish or brownish grays (Field 1) which are less prominently tinged than is the case with gas blacks, but which are in decided contrast to the nearly neutral gray of the heavy lampblacks (Field 3) or the closely related "Thermax."

It is to be inferred from the differences in the total illumination of the three fields that the covering power of the black pigments with respect to white light passes through an optimum. As is also the case with other powdered coloring agents, the optimum is obtained with a black of intermediate fineness, a fact which would not be revealed by the ordinary determinations of the black content of a rubber mix.

In the same manner, dark field examination may be used for the study of stocks containing various grades of golden antimony, although in such cases the various colors of the individual particles themselves lead to a mottled effect in the field as a whole. This effect is illustrated in Figures 32 and 33, Plate VII, which show the appearance of thin sections of two automobile inner tubes of the older, accelerator-free type. The different degrees of fineness of the antimony pentasulfides used can be recognized from these pictures. Field 1 shows a very finely divided grade of German origin, whereas a somewhat less fine and more luminous grade of American manufacture is illustrated in Field 2. As is also to be seen in the bright field photograph (Fig. 15, Plate V), the German product is predominantly submicroscopic. A comparison of the transmitted colors (Fields 8 and 9 of Figure 28) indicates that the American pigment is not as fine as the German, since the mix containing the former does not transmit reddish-yellow light as well as that

containing the latter. The conclusion from this comparison can be confirmed by a comparison in the dark field, although a numerical determination of the relative particle density is not possible. The pictures (made with somewhat reduced light) show that the German pigment consists very largely of particles which scatter blue and violet, while the American product consists of a mixture of particles (both reddish-yellow and bluish-green). In other words, there is only a little blue color in the picture obtained in the latter case, and that little is exclusively a mixture of blue and green. The results do not reveal whether the American product, which is primarily composed of particles of two different degrees of dispersion, was prepared by fractional precipitation or by the mixing of two separate precipitates. The differences in the total luminosity of the two dark field pictures indicates that the German pigment is inferior to the American in the matter of coloring power. (*See* p. 664.)

A satisfactory picture of a stock containing various pigments can only be obtained when the stock contains no submicroscopic particles. In such a case, dark field examination can serve as a negative test to demonstrate with certainty that small quantities of "active" pigments, such as gas black or antimony pentasulfide, are not present. The dark field picture obtained with a solid tire stock is shown in Figure 30, Plate VII. It is apparent that the stock contains only zinc oxide and lampblack of a low degree of fineness, since there is no evidence whatever of luminosity of the rubber matrix as a consequence of embedded finer particles. Although the zinc oxide and lampblack have approximately the same degrees of fineness, they are readily to be distinguished from each other on the basis of their different luminosities. A noticeable blue radiation, which is observed as a "halo" around the coarser particles of zinc oxide, seems to decrease in intensity as a consequence of the interaction of zinc oxide and accelerator. It is not noticeable during subjective observation.

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Compiled by H. P. Albaugh

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INTRODUCTION

The tremendous advances made within the rubber industry during the past century are indicated by the growth of the literature on the subject. The following inclusive bibliography of books and pamphlets permits a survey of the rapid increase in rubber publications of this type, to the end of 1933.

In order to facilitate reference by either subject or author, the entries have been arranged under subject and indexed by author. The subject groupings used are listed in the table of contents, while the alphabetical author index is incorporated in the general author index to the volume. Each entry in the bibliography includes, so far as such data could be located, the author's name, title in full, series, place of publication, publisher, date, paging, and a review reference. The paging may be inaccurate because of disagreement in the sources consulted, but it has been included as an indication of the scope of the publication. Notes of illustrations and bibliographies contained in individual books are usually not given at all, because they could not be given uniformly.

Lack of space forbade the inclusion of annotations. Therefore, descriptive review references have been noted whenever they could be found, and the sources of some of the references which could not be verified are given. Since the bibliography is inclusive, not all the publications listed are of equal worth, but it is hoped that the review references may be of assistance in their evaluation. Review references are omitted for most of the U. S. government publications, and for several of the longer series [Ceylon Dept. of Agriculture Bulletins, Federated Malay States Dept. of Agriculture Bulletins, Rubber Research Scheme (Ceylon) Bulletins] of which the numbers pertaining to rubber are listed for convenient reference.

In general, the aim has been to include all books and pamphlets of any informational value pertaining to rubber and allied substances. Journal references and reprints (unless published and sold in book or pamphlet form) have been excluded. Space limitations have not permitted the inclusion of general chemical, analytical, travel, and encyclopedic material not relating chiefly to rubber. Lists of rubber journals and abstract journals and current patent sources are given at the end of the bibliography, together with a partial list of firms publishing more or less informative material on rubber and compounding materials.

The publications relating to rubber, as well as the bibliographic tools, in the collections of the Firestone Tire and Rubber Company Libraries, Akron Public Library, the Library of the Municipal University of Akron, and Cleveland Public Library, were consulted. Review and other references were obtained from the following periodicals: Chemical Abstracts, Gummi-Zeitung (1920-date), India Rubber World (1899-date), Industrial and Engineering Chemistry, Kautschuk, Rubber Age (London), Rubber Age (New York), and Rubber Chemistry and Technology. The U. S. Catalog of Public Documents was searched, as well as the book trade indexes of the various countries (Catalogue de la Librairie Francaise, Deutsches Bücherverzeichnis, English Catalogue of Books, American Catalog, U. S. Catalog, and Cumulative Book Index) and the catalog of books pertaining to rubber, etc., in the library of the Koloniaal Instituut te Amsterdam.

After most of the other sources named had been searched, the 1927 Library Catalogue of the Research Association of British Rubber Manufacturers ("RABRM") was received and checked. Just before the bibliography went to press, Mr. T. R. Dawson and Mr. B. D. Porritt of the Research Association of British Rubber Manufacturers responded very generously to a further inquiry by sending the monthly lists of books and other material added to the RABRM Library since the appearance of the 1927 Library Catalogue, as well as a copy of their "want list" and lists of RABRM publications. When these sources were checked, some 350 additional titles not noted elsewhere were obtained, excluding over 300 titles of RABRM publications and amplified collation data for titles which had already been included. The titles found only in RABRM lists are indicated by the initials "RABRM," in parentheses, and those from the catalogs of the Koloniaal Instituut te Amsterdam by "KI." Some idea of the wealth of rubber literature collected in the RABRM Library may be conveyed by the statement that of the 1,746 titles entered in the following bibliography, only about 200 were not found in a rapid check of the RABRM lists. It is believed, however, that the following bibliography is the most complete compilation of references to books and pamphlets on the cultivation, properties, and uses of rubber and allied substances ever published in one place, and it is hoped that the omissions which seem inevitable in a work of this kind will be both few and unimportant. If this bibliography aids in correlating the advances already made in the "science of rubber" with those yet to come, it will have served its purpose.

Especial thanks are due to the staff of the Research Association of British Rubber Manufacturers for their cooperation in this venture. It is also a pleasure to acknowledge the willing assistance of the staff members of the various other libraries consulted, in making accessible the rubber publications and bibliographic tools in their charge.

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ACCELERATORS

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See also: CHEMISTRY; SPECIFICATIONS.

ANTIOXIDANTS

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BALATA

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272—Permeation of oxygen breathing apparatus by gases and vapors, by A. C. Fieldner, S. H. Katz and S. P. Kinney. 1921. 24 p.

292—Tests of gas masks and respirators for protection from locomotive smoke in railroad tunnels, with analysis of tunnel atmosphere; by A. C. Fieldner, S. H. Katz, and S. P. Kinney. 1922. 27 p.

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Bradley, H., and **Hancock, C. C.** Modern roadmaking. (With a chapter on rubber roadways.) London, Contractors' Record, Ltd., 1928. 344 p. [*Rubber Age (London)* **9**, 172 (1928)].

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See also: LATEX: Rubber Growers' Association, Inc., "Digest of patents," etc.

TIRES

See: TIRES.

VULCANIZATION

See: CHEMISTRY; GENERAL; TECHNOLOGY

JOURNALS

PERIODICAL PUBLICATIONS DEVOTED CHIEFLY TO RUBBER

Archief voor de Rubbercultuur in Nederlandsch-Indië.
In this journal are published the following series of communications:
Mededeelingen van het Algemeen Proefstation der Algemeene Vereeniging van Rubberplanters ter Oostkust van Sumatra. (Both General Series and Rubber Series.)
Mededeelingen van het Proefstation West-Java.
Mededeelingen van het Proefstation voor Rubber.
Mededeelingen van den Vorlichtingsdienst voor Zuid en West-Sumatra.
Mededeelingen van het Besoekisch Proefstation.
Etc.
Bulletin of the Rubber Growers' Association.
Le Caoutchouc & la Gutta-Percha.
La Goma (Spanish).
Gummi-Zeitung.
*Home and Colonial Mail (The Tea and Rubber Mail).
India Rubber and Tire Review.
India Rubber Journal.
India Rubber World.
*Industrial and Engineering Chemistry (Regular and Analytical Editions).
Institution of the Rubber Industry. Transactions.
Journal of the Rubber Industry, U. S. S. R. (In Russian). (Shurnal resinowoi promyschlennosti.)

Journal of the Rubber Research Institute of Malaya.
Journal of the Rubber Society, Japan (Gomei) (In Japanese).
Kautschuk.
*Malayan Agricultural Journal.
*Malayan Tin and Rubber Journal.
Netherlands Indian Rubber Trade Association at Batavia. Maandelijksche rubberstatistieken van Ned. Oost Indië. (Rubber statistics of the Dutch East Indies) Monthly (Text in English and Dutch).
Research Association of British Rubber Manufacturers. Journal. (Published in same cover with their Summary of Current Literature.)
Research Association of British Rubber Manufacturers. Rubber Economic Intelligence. (Vol. 1, No. 1, Oct., 1933.)
Revue Generale du Caoutchouc.
Rickinson, W. H. & Son.
Rubber companies' position (monthly).
World's rubber position (monthly).
Rubber Age (London).
Rubber Age (New York).
Rubber Chemistry and Technology (Reprints, abstracts, and translations).
Rubber Research Scheme (Ceylon). Quarterly circulars. (Popular summaries of work described in detail in their bulletins).
Rubber World (Gomu Sekai) (In Japanese).
Soviet Soviet Kautschuk (In Russian).
*Tropical Agriculturist (The Agricultural Journal of Ceylon).
Wijnand & Keppler's Rubberbericht (Amsterdam).
*Not limited to rubber, but containing many valuable articles on rubber.

See also: List of abbreviations used in this book, for various planting publications issued serially but not listed above. Occasional articles on rubber appearing in various other journals from time to time are abstracted in the abstract journals listed below. The "List of Periodicals Abstracted," issued by Chemical Abstracts in 1931, gives publishers, prices, etc. for most of the above journals.

ABSTRACT JOURNALS WHICH ABSTRACT ARTICLES ON RUBBER

Chemical Abstracts.
Chemisches Zentralblatt.
Chimie et Industrie.
Journal of the Society of Chemical Industry (containing British Chemical Abstracts B).
Research Association of British Rubber Manufacturers. Information Bureau. Summary of Current Literature.

CURRENT PATENT SOURCES

British Patent Abstracts. Series C. (Published in 16-page sections for each group, as a sufficient number of abstracts are accumulated.)
Group V—India-rubber and gutta-percha.
Group XXXIV—Wheels for vehicles, including wheel tyres, pneumatic.
Canadian Patent Office Record.
German Patentblatt und Auszüge aus den Patentschriften.
Rubber Patent and Trade Mark Review (issued by RABRM, beginning Jan., 1934).
U. S. Patent Office. Official Gazette.
(For patents of other foreign countries, consult the abstracts of the patents given in the abstract journals listed above. The French patent journal does not give abstracts.)

PARTIAL LIST OF FIRMS PUBLISHING MORE OR LESS INFORMATIVE ADVERTISING BULLETINS, ETC., ON RUBBER AND COMPOUNDING INGREDIENTS

American Instrument Co., Inc.
American Zinc Sales Co.
Binney & Smith Co.
British Aluminum Co., Ltd.
Godfrey L. Cabot, Inc.
Dunlop Rubber Co., Ltd.
E. I. du Pont de Nemours & Co., Inc.
Firestone Tire & Rubber Co.
B. F. Goodrich Co.
Goodyear Tire & Rubber Co.
Graesser-Monsanto Chemical Works, Ltd.
C. P. Hall Co.
J. M. Huber, Inc.
I. G. Farbenindustrie (also through J. M. Steel & Co., Ltd.).
Imperial Chemical Industries, Ltd.
R. J. King & Co.
Monsanto Chemical Co.
Naugatuck Chemical Co.
New Jersey Zinc Co.
Revertex Corp. of America.
Robinson Bros., Ltd.
Rubber Service Laboratories Co.
L. Schopper, Leipzig (Testing Machines, Inc., N. Y.)
Henry L. Scott Co.
Simplex Wire & Cable Co.
Stamford Rubber Supply Co.
Thiokol Corp.
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